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(54) **Transition metal complex catalyzed reactions.**

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Description

This invention relates to rhodium complex catalyzed hydroformylation reactions using diorganophosphite ligands as well as to corresponding rhodium-diorganophosphite ligand complexes employed therein.

It is well known in the art that carbonylation reactions are enhanced by the use of a modified Group VIII metal catalysts e.g., catalysts comprising a Group VIII transition metal-phosphorus ligand complex.

Carbonylation processes directed to production of oxygenated products in the presence of a catalyst in general involve the reaction of an organic compound with carbon monoxide and preferably another reactant, especially hydrogen, and are well known in the art, e.g., see J. Falbe, "New Synthesis With Carbon Monoxide" Springer Verlag, New York 1980. Such processes may include the carbonylation of organic compounds such as olefins, acetylenes, alcohols and activated chlorides with carbon monoxide alone or with carbon monoxide and either hydrogen, alcohol, amine or water, as well as ring closure reactions of functional unsaturated compounds e.g. unsaturated amides with CO. One of the major types of known carbonylation reactions is the hydroformylation of an olefinic compound with carbon monoxide and hydrogen to produce oxygenated products such as aldehydes using a Group VIII transition metal-phosphorus ligand complex wherein the phosphorus ligand is a triorganophosphine or triorganophosphite, followed by a subsequent aldolization reaction if desired.

It is further well known that the phosphorus ligand employed in such catalyzed carbonylation processes may have a direct effect on the success of such a given process. Moreover, while it is evident that the selection of the particular phosphorus ligand to be used in any such transition metal catalyzed carbonylation process depends in the main on the end result desired, the best overall processing efficiency may require a compromise selection among numerous factors involved, for it is known that not all phosphorus ligands will provide identical results with regard to all factors under all conditions. For example, in hydroformylation such factors as product selectivity, catalyst reactivity and stability, and ligand stability are often of major concern in the selection of the desired phosphorus ligand to be employed. Moreover, such a selection may also depend on the olefinic starting material involved in the hydroformylation process, since all olefins do not have the same degree of reactivity under all conditions. For instance, internal olefins and sterically hindered alpha olefins e.g. isobutylene, are in general much less reactive than sterically unhindered alpha olefins.

Thus, e.g. by tailoring of the metal-phosphorus ligand complex catalyst, specific desired results for the product, the process and/or catalyst performance may be obtained. For example, US-A- 3,527,809 teaches how alpha olefins can be selectively hydroformylated with rhodium-triorganophosphine or triorganophosphite ligand complexes to produce oxygenated products rich in normal aldehydes, while US-A- 4,148,830 and 4,247,486 disclose both liquid and gas recycle operations directed to the same result using a rhodium-triphenylphosphine ligand complex catalyst. US-A-4,283,562 discloses that branched-chain alkylphenylphosphine or branched-chain cycloalkylphenylphosphine ligands can be employed in a rhodium catalyzed hydroformylation process of olefin to produce aldehydes in order to provide a more stable catalyst against entrinsic deactivation while retarding the rate of the hydroformylation reaction far less than n-alkyldiphenylphosphine ligands, relative to that obtained using triphenylphosphine. US-A- 4,400,548 discloses that bisphosphine monooxide ligands can be employed to provide rhodium complex catalysts of improved thermal stability useful for the hydroformylation production of aldehydes.

EP-A-96988 and 96986 teach the use of, among others, (bi)cyclic phosphites in the rhodium catalyzed hydroformulation of internal olefins and alpha-olefins, respectively.

However, despite the obvious benefits attendent with the prior art references mentioned above, the search for a more effective phosphorus ligand which will provide a more active, more stable and/or more all purpose type metal-phosphorus ligand complex catalyst is a constant one in the art and heretofore, unlike the present invention, has been centered for the most part on the use of triorganophosphine and triorganophosphite ligands.

Disclosure of Invention

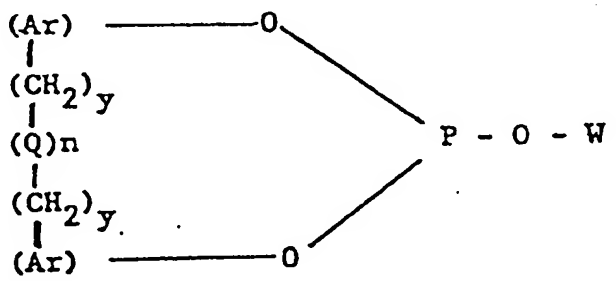
It has now been discovered that certain diorganophosphites (some of which are already known as stabilizers and/or antioxidants for organic polymers, see EP-A-2821 and 9115) may be employed as the phosphorus ligand in rhodium complex catalyzed hydroformylation processes to provide numerous advantages relative to heretofore commonly proposed rhodium-phosphorus ligand complex catalysts.

For instance, the diorganophosphite ligands employable herein are useful in providing both improved catalytic activity and at the same time improved catalyst and ligand stability in hydroformylation, even with

less reactive olefins such as isobutylene and internal olefins. For example, the high catalytic activity provided by the diorganophosphite ligands allows one to carry out the hydroformylation of olefins at lower temperatures than generally preferred when conventional ligands such as triorganophosphines are employed. Likewise, in the hydroformylation of olefins enhanced ligand and catalyst stability against inherent side reactions, such as stability against reacting with the aldehyde product, hydrolytic stability and stability against hydrogenolysis of the ligand may be achieved by the use of the diorganophosphite ligands relative to the use of triorganophosphite ligands. Further, the use of the diorganophosphite ligands employable herein provides an excellent means for controlling product selectivity in hydroformylation reactions. For example, the diorganophosphites have been found to be very effective ligands when oxygenated products, e.g. aldehydes, having very low normal to iso (branched) product ratios are desired. Moreover, the diorganophosphite ligands employable herein have not only been found to provide excellent catalyst activity and both catalyst and ligand stability in the hydroformylation of sterically unhindered alpha olefins, as well as less reactive type olefins, such as sterically hindered alpha olefins e.g. isobutylene, and internal olefins, but have also been found to be especially useful in providing such catalyst activity and both catalyst and ligand stability when hydroformylating mixed alpha olefin and internal olefin starting materials.

Thus it is an object of this invention to provide an improved hydroformylation process, wherein said process is carried out in the presence of a rhodium-diorganophosphite ligand complex catalyst. It is also an object of this invention to provide a novel class of rhodium-diorganophosphite ligand complexes suitable for use in such hydroformylation processes. Other objects and advantages of this invention will become readily apparent from the following written description and appended claims.

Accordingly, a generic aspect of this invention can be described as a hydroformylation process for producing aldehydes which comprises reacting an olefinically unsaturated organic compound with carbon monoxide and hydrogen in the presence of a rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and a diorganophosphite ligand, and in the added presence of a free diorganophosphite ligand, characterized in that the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand are each individually ligands having the formula



(I)

wherein each y individually has a value of 0 or 1; n has a value of 0 or 1; Q is a divalent bridging group selected from $-CH_2-$, $-CH(CH_3)-$ and -S-;

W is an unsubstituted or substituted C_1-C_{18} alkyl or an unsubstituted or substituted C_6-C_{18} aryl group; and each Ar represents an identical or different unsubstituted or substituted aryl group selected from phenylene, naphthylene and anthracylene;

said substituent(s) on W and Ar being selected from C_1-C_{18} alkyl groups , phenyl, naphthyl, benzyl, phenylethyl, tolyl, xylyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, halogen, nitro, cyano, trifluoromethyl, hydroxy, $-Si(R^6)_3$, $-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$ $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$ wherein R^6 individually represents the same or different hydrocarbon groups selected from C_1-C_{18} alkyl groups and aryl, aralkyl, alkaryl and alicyclic groups containing from 6 to 18 carbon atoms with the proviso that in substituents $-N(R^6)_2$ each R^6 taken together can also represent a divalent bridging group that forms a heterocyclic group with the nitrogen atom and in substituents $-N(R^6)_2$,$-C(O)N(R^6)_2$ and $-N(R^6)C(O)R^6$ each R^6 bonded to N can also be hydrogen while in substituents $-P(O)(R^6)_2$ one R^6 can also be hydrogen; said Ar groups being bonded through the ortho positions in relation to the oxygen atoms that connect the Ar groups to the phosphorus atom; and any substituent, when present on such Ar groups or an aryl group W, being bonded in the para and/or ortho position of the aryl group in relation to the oxygen atom that bonds the given substituted aryl group to the phosphorus atom,

provided that in case W is an aryl group at least one of said aryl groups Ar and W is substituted and not all of the total accumulative number of ortho positions on Ar and W are substituted with a radical having a

steric hindrance of isopropyl or greater.

Another generic aspect of this invention comprises certain diorganophosphite ligands and catalyst precursor solutions as described more fully herein below.

As seen by the above formula the diorganophosphite ligands employable herein represent an entirely different class of compounds than triorganophosphite ligands. The diorganophosphites employable herein contain only two organic radicals bonded to the phosphorus atom through oxygen, one of said organic radicals being bonded through two phenolic oxygen atoms (wherein each oxygen atom is bonded to a separate aryl radical) and the other organic radical through a single phenolic or alcoholic oxygen atom. Triorganophosphites contain three organic radicals each radical being bonded to the phosphorus atom through its own individual oxygen atom. Thus if hydrolyzed, the diorganophosphite ligands employable herein would yield both a diphenolic compound in which each phenolic oxygen atom is bonded to a separate aryl radical, and a mono-ol compound, while triorganophosphite ligands would yield the equivalent of three mono-ol compounds.

The aldehydes produced by the process of this invention correspond to the compounds obtained by the addition of a carbonyl group to an olefinically unsaturated carbon atom in the starting material with simultaneous saturation of the olefinic bond. Such hydroformylation processes are known in industry also under other names such as the oxo process or reaction, oxonation and the Roelen reaction. Accordingly, the processing techniques of this invention may correspond to any of the known processing techniques heretofore employed in conventional hydroformylation reactions.

For instance, the preferred hydroformylation process can be conducted in continuous, semi-continuous, or batch fashion and involve a liquid recycle and/or gas recycle operation as desired. Likewise, the manner or order of addition of the reaction ingredients, catalyst and solvent are also not critical and may be accomplished in any conventional fashion.

In general, the preferred hydroformylation reaction is preferably carried out in a liquid reaction medium that contains a solvent for the catalyst, preferably one in which both the olefinically unsaturated compound and catalyst are substantially soluble. In addition, as is the case with prior art hydroformylation processes that employ a rhodium-phosphorus complex catalyst and free phosphorus ligand, the hydroformylation process of this invention is effected in the presence of free diorganophosphite ligand as well as in the presence of the complex catalyst. By "free ligand" is meant diorganophosphite ligand that is not complexed with the rhodium atom in the active complex catalyst.

The hydroformylation process of this invention is an improved selective hydroformylation over those known Group VIII transition metal-phosphorus ligand complex catalyzed hydroformylation reactions due to the improved catalyst reactivity as well as simultaneous improved catalyst and ligand stability, and other benefits, afforded by the use of the diorganophosphite ligands employable herein, as opposed to the triorganophosphine and triorganophosphite ligands heretofore employed in the prior art.

It is to be noted that the successful practice of this invention does not depend and is not predicated on the exact structure of the catalytically active metal complex species, which may be present in their mononuclear, dinuclear and or higher nuclearity forms. Indeed the exact active structure is not known. Although it is not intended herein to be bound to any theory or mechanistic discourse, it appears that the active catalytic species may in its simplest form consist essentially of rhodium in complex combination with the carbon monoxide and a diorganophosphite ligand.

The term "complex" as used herein and in the claims means a coordination compound formed by the union of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which is also capable of independent existence. The diorganophosphite ligands employable herein which possess the element phosphorus have one available or unshared pair of electrons and thus are capable of forming a coordinate bond with the rhodium. As can be surmised from the above discussion, carbon monoxide (which is also properly classified as a ligand) is also present and complexed with the rhodium. The ultimate composition of the active complex catalyst may also contain an additional organic ligand or anion satisfying the coordination sites or nuclear charge of the rhodium as in the case of heretofore conventional Group VIII transition metal-triorganophosphine or phosphite catalysts. Illustrative additional organic ligands and anions include e.g. hydrogen$^-$ (H^-), alkyl$^-$, aryl$^-$, substituted aryl$^-$, CF_3^-, $C_2F_5^-$, CN^-, R_2PO^- and $RP(O)(OH)\ O^-$ (wherein each R is alkyl or aryl), acetate$^-$, acetylacetonate$^-$, PF_4^-, PF_6^- NO_2^-, NO_3^-, CH_3O^-, $CH_2=CHCH_2^-$, C_6H_5CN, CH_3CN, NO, NH_3, pyridine, $(C_2H_5)_3N$, mono-olefins, diolefins and triolefins, tetrahydrofuran, and the like. It is of course to be understood that the active complex species is preferably free of any additional organic ligand or anion that might poison the catalyst and have an undue adverse effect on catalyst performance. For instance it is known that in conventional rhodium catalyzed hydroformylation reactions that halogen anions and sulfur compounds can poison the catalyst. Accordingly it is preferred that in the (rhodium catalyzed) hydrofor-

mylation reactions of this invention the active catalysts also be free of halogen and sulfur directly bonded to the rhodium.

The number of available coordination sites on rhodium is well known in the art and may range in number from 4 to 6. By way of illustration it appears that the active rhodium catalyst species of this invention contains, in its simplest form, an amount of diorganophosphite ligand and carbon monoxide equal to a total of four moles in complex combination with one mole of rhodium. Thus the active species may comprise a complex catalyst mixture, in their monomeric, dimeric or higher nuclearity forms, which are characterized by one, two, and/or three diorganophosphite molecules complexed per one molecule of rhodium. As noted above carbon monoxide is also present and complexed with the rhodium in the active species. Moreover, as in the case of conventional rhodium-triorganophosphine or phosphite ligand complexed catalyzed hydroformylation reactions, the active catalyst species of which is generally considered to also contain hydrogen directly bonded to the rhodium, it is likewise considered that the active species of the rhodium catalyst employed in this invention during hydroformylation may also be complexed with hydrogen in addition to the diorganophosphite and carbon monoxide ligands, particularly in view of the hydrogen gas employed in the process.

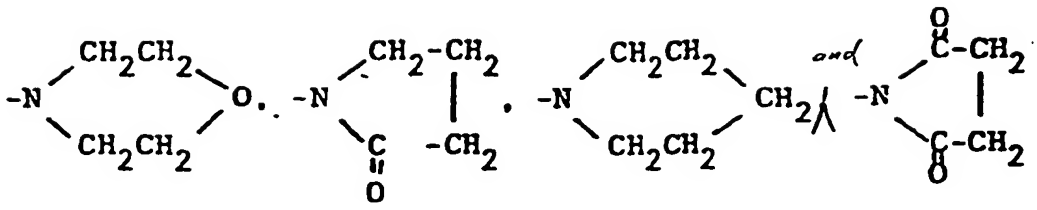
Moreover, regardless of whether one preforms the active complex catalyst prior to introduction into the hydroformylation reaction zone or whether the active species is prepared in situ during the hydroformylation reaction, the hydroformylation reaction is effected in the presence of free diorganophosphite ligand. Thus by way of illustration the ultimate composition of the preferred active rhodium complex species catalyst can be likened or attributable to the outcome of competing reactions between carbon monoxide and the diorganophosphite ligands for complexing or coordination sites with the rhodium element. These competing reactions can be disturbed or influenced, within significant limits, by increasing or decreasing the concentration of the diorganophosphite ligand. As a generalized statement, the component (carbon monoxide or diorganophosphite ligand) which can shift the equilibrium of the competing reaction in its favor should enjoy the greater opportunities of occupying the coordination or complexing sites. For example, one may view the function of free diorganophosphite ligand as either maintaining the status quo of the various forms of active complex catalyst during the hydroformylation, or as a means for shifting the equilibrium of the competing reactions in its favor and therefore causing additional diorganophosphite ligands to enter into complex combination with rhodium with the probable eviction of a similar number of carbon monoxide ligands from the complex catalyst.

The diorganophosphite ligands employable in this invention are those of formula (I) above.

Specific illustrative monovalent hydrocarbon groups represented by W include primary, secondary and tertiary alkyl groups such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, t-butylethyl, t-butylpropyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, 2-ethylhexyl, decyl and octadecyl; and aryl groups such as phenyl, naphthyl and anthracyl. Preferably the unsubstituted alkyl groups contain from 1 to 10 carbon atoms.

Preferably the substituent groups on Ar and W, including those represented by R^6, are unsubstituted alkyl or aryl groups.

Among the more specific alkyl groups, including those represented by R^6, that may be bonded to the monovalent hydrocarbon groups represented by W and/or the Ar groups of the above diorganophosphite formula that may be mentioned are primary, secondary and tertiary alkyl groups such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, t-butylethyl, t-butylpropyl, n-hexyl, amyl, sec-amyl, t-amyl, isooctyl and decyl. Other illustrative hydrocarbon groups R^6 are phenyl, naphthyl, benzyl, phenylethyl, tolyl, xylyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl and cyclohexylethyl. More specific illustrative non-hydrocarbon substituents that may be present on the monovalent hydrocarbon groups represented by W and/or the Ar groups of the above diorganophosphite formula include e.g. halogen, preferably chlorine or fluorine, $-NO_2$, $-CN$, $-CF_3$, $-OH$, $-Si(CH_3)_3$, $-Si(OCH_3)_3$, $-Si(C_3H_7)_3$, $-C(O)CH_3$, $-C(O)C_2H_5$, $-OC(O)C_6H_5$, $-C(O)OCH_3$,$-N(CH_3)_2$, $-NH_2$, $-NHCH_3$, $-NH(C_2H_5)$, $-CONH_2$, $-CON(CH_3)_2$, $-S(O)_2C_2H_5$, $-OCH_3$, $-OC_6H_5$, $-C(O)C_6H_5$, $-O(t\text{-}C_4H_9)$, $-SC_2H_5$, $-OCH_2CH_2OCH_3$, $-(OCH_2CH_2)_2OCH_3$, $-(OCH_2CH_2)_3OCH_3$, $-SCH_3$, $-S(O)CH_3$, $-SC_6H_5$, $-P(O)(C_6H_5)_2$, $-P(O)(CH_3)_2$, $-P(O)(C_2H_5)_2$, $-P(O)(C_3H_7)_2$, $-P(O)(C_4H_9)_2$, $-P(O)(C_6H_{13})_2$, $-P(O)CH_3(C_6H_3)$, $-P(O)(H)(C_6H_5)$, $-NHC(O)CH_3$,



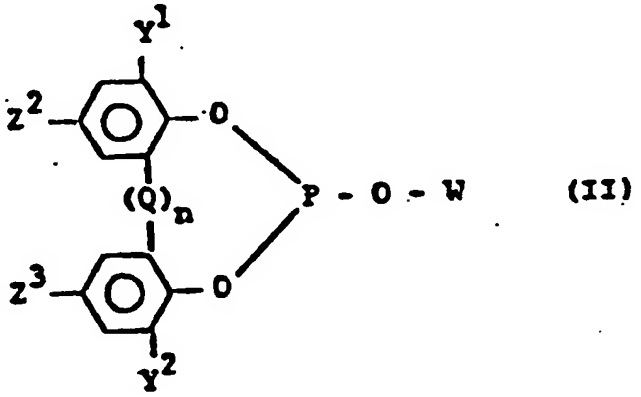
and the like. In general, the substituent groups present on the groups represented by W and the Ar groups of the above diorganophosphite formula contain from 1 to 15 carbon atoms.

Moreover, each Ar group and/or group represented by W may contain one or more such substituent groups which substituent groups may also be the same or different in any given diorganophosphite.

A preferred class of diorganophosphite ligands employable herein are those wherein W is a substituted or unsubstituted C_1-C_{18} alkyl group. Preferred alkyl groups contain from 1 to 10 carbon atoms, such as those defined above. Other preferred alkyl groups are substituted with a non-hydrocarbon substituent as discussed above, i.e., $-Si(R^6)_3$, $-Si(OR^6)_3$; $-C(O)R^6$; $-C(O)OR^6$; $-OC(O)R^6$; $-C(O)N(R^6)_2$ and $-N(R^6)C(O)R^6$; $-S(O)_2R^6$; $-S(O)R^6$; $-OR^6$; $-SR^6$; and $-P(O)(R^6)_2$, wherein R^6 is the same as defined above, as well as halogen, nitro, cyano, trifluoromethyl and hydroxy groups. An electro-negatively substituted alkyl group has the potential of forming a weak coordinate bond with the rhodium complex, and such substi-tuents may render the rhodium-diorganophosphite complex catalyst in hydroformylation more catalytically stable. The most preferred electro-negatively substituted alkyl groups are those of the formula $[C(R^7)_2]_pP(O)(R^6)_2$ wherein each R^6 is selected from C_1-C_{18} alkyl, phenyl and cyclohexyl, each R^7 is individually the same or different and is selected from hydrogen and C_1-C_4 alkyl groups and p has a value of 1 to 10, especially $-(CH_2)_pP(O)(R^6)_2$ groups wherein p is 1 to 3 and each R^6 is individually the same or different and is as defined above, with the proviso that one R^6 group can also be hydrogen.

Such types of diorganophosphite ligands employable in this invention and/or methods for their preparation are well known. For instance a conventional method for preparing such ligands comprises reacting a corresponding organic diphenolic compound (e.g. 2,2'-dihydroxybiphenyl) with phosphorus trichloride to form an organic phosphorochloridite intermediate (e.g. 1,1'-biphenyl-2,2'diyl-phosphorochloridite) which in turn is reacted with a corresponding mono-hydroxy compound (e.g. 2,6-di-t-butyl-4-methylphenol) in the presence of an HCl acceptor, e.g. an amine, to produce the desired diorganophosphite ligand [e.g. 1,1'-biphenyl-2,2'-diyl-(2,6-di-t-butyl-4-methylphenyl)phosphite]. Optionally, these ligands may also be prepared in the reverse order, for instance, from a preformed organic phosphorodichloridite (e.g. 2,6-di-t-butyl-4-methylphenyl phosphorodichloridite) and a corresponding diphenolic compound (e.g. 2,2'-dihydroxybiphenyl) in the presence of an HCl acceptor, e.g. an amine, to produce the desired diorganophosphite ligand, [e.g. 1,1'-biphenyl-2,2'-diyl-(2,6-di-t-butyl-4-methylphenyl)phosphite].

A further preferred class of diorganophosphite ligands employable in this invention is that of the formula



(II)

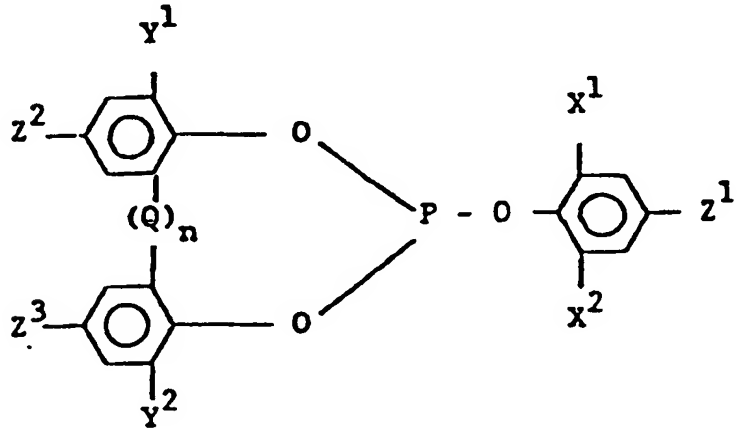
wherein Q is $-CH_2-$ or $-CHCH_3-$; n is 0 or 1; each Y^1, Y^2, Z^2 and Z^3 group individually represents hydrogen or a group given above as possible substituent on Ar and W (preferred alkyl groups having from 1 to 8 carbon atoms), with the proviso that both Y^1 and Y^2 are groups having a steric hindrance of isopropyl, or more preferably t-butyl, or greater, and wherein W represents an alkyl group having from 1 to 18 carbon

atoms, preferably from 1 to 10 carbon atoms. The preferred ligands are those of Formula (II) above, wherein both Y^1 and Y^2 are branched chain alkyl groups having three to five carbon atoms, especially t-butyl, Z^2 and Z^3 are hydrogen or an alkyl group, especially t-butyl.

Another preferred class of diorganophosphite ligands employable herein are those wherein W is a substituted or unsubstituted aryl radical such as defined above, especially substituted or unsubstituted phenyl radicals.

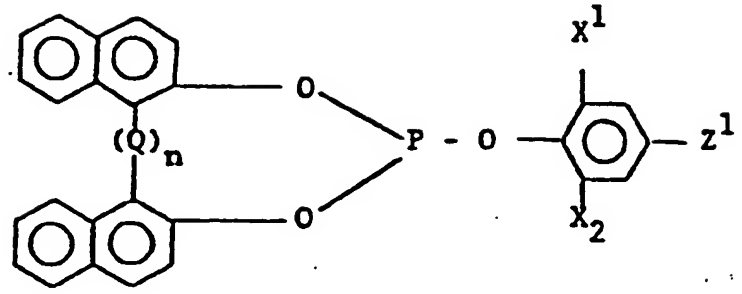
It has been observed that in rhodium catalyzed hydroformylation reactions, when the diorganophosphite ligand employed is one in which W represents an aryl radical, that substitution (excluding any substitution caused by the bridging group $-(CH_2)_y-(Q)_n-(CH_2)_y-$) of the ortho position of the aryl group (W) and the two Ar groups of Formula (I), i.e. those positions relative to the oxygen atom that bond each aryl group to the phosphorus atom of the diorganophosphite ligand may influence the catalytic activity and/or stability of the ligand. Apparently steric hindrance around the phosphorus atom of the diorganophosphite ligand caused by substitution in such ortho positions of all the aryl groups has an influence on ligand stability and/or catalytic activity, particularly with regard to hydroformylations carried out in the presence of excess free diorganophosphite ligand. For instance, diorganophosphite ligands in which all the aryl groups are unsubstituted aryl radicals (too little steric hindrance) and diorganophosphite ligands in which four of the total accumulative number of such ortho positions on the aryl groups are substituted with a radical having a steric hindrance of isopropyl or greater, (too much steric hindrance), are not considered desirable because of the poor ligand stability and/or catalytic activity that may be obtained with their use particularly in the presence of excess free ligand. On the other hand improved ligand stability and/or catalytic activity in rhodium catalyzed hydroformylation even in the presence of excess free ligand may be obtained when at least two of the total accumulative number of such ortho positions on all the aryl groups of the diorganophosphite ligand are substituted with a substituent radical having a steric hindrance of isopropyl, or more preferably t-butyl, or greater, provided that no more than three and preferably not more than two of the total accumulative number of such ortho positions on all the aryl groups are substituted with a radical having a steric hindrance of isopropyl or greater at the same time. In addition, diorganophosphite ligands in which two such available ortho positions of the two Ar groups of generic Formula (I) above are substituted with a radical having a steric hindrance of isopropyl, or more preferably t-butyl, or greater, appear to possess better ligand stability as a general rule than if the diorganophosphite ligands were so substituted in the two such available ortho positions of the aryl group represented by W. Moreover, in the preferred diorganophosphite ligands, the catalytic activity and/or stability may be further enhanced if one of said ortho positions of the aryl radical represented by W is substituted with an electro-negative substituent, e.g. cyano, having the capability of forming a weak coordinate bond with rhodium.

Thus another preferred class of diorganophosphite ligands employable in this invention are those of the formulas



(III)

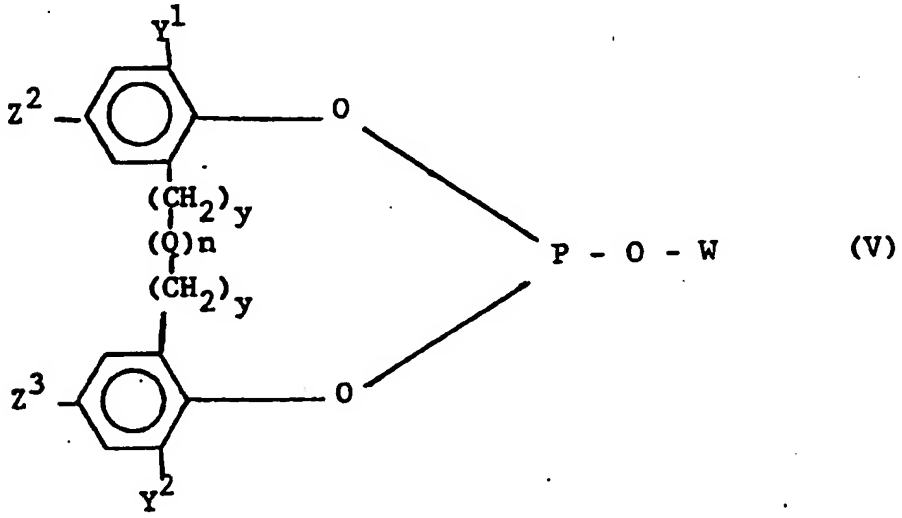
and



(IV)

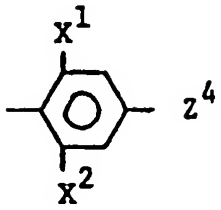
wherein Q is $-CH_2-$ or $-CHCH_3-$; n has a value of 0 or 1; each X^1, X^2, Y^1, Y^2, Z^1, Z^2, and Z^3 group individually represents hydrogen, or one of the groups given above as possible substituents on Ar and W (the preferred alkyl groups having from 1 to 8 carbon atoms), with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite of Formulae (III) and (IV) above are radicals having a steric hindrance of isopropyl, or more preferably t-butyl, or greater, and with the proviso that in Formula (III) above no more than three and preferably no more than two of the X^1, X^2, Y^1, or Y^2 groups are groups having a steric hindrance of isopropyl or greater at the same time. Preferably the X^1, X^2, Y^1, and Y^2 groups are branched chain alkyl groups having 3 to 5 carbon atoms, especially t-butyl. The more preferred ligands in Formula (III) are those wherein either both Y^1 and Y^2 groups are t-butyl or both X^1 and X^2 groups are t-butyl.

Yet another preferred class of diorganophosphite ligands, which are considered to be novel compositions of matter per se, employable in this invention are those of the formula



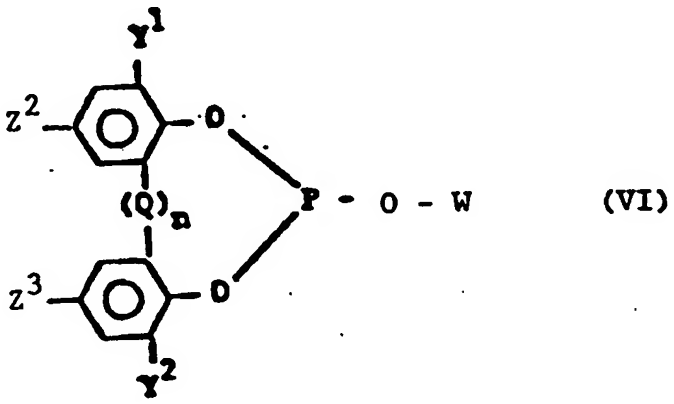
(V)

wherein Z^2 and Z^3 each individually represent a radical selected from hydroxy (-OH) and an ether (i.e. oxy) group $-OR^6$ wherein R^6 is the same as defined above and wherein W, Y^1, Y^2, Q, n and y are the same as defined above, preferred alkyl groups Y^1 and Y^2 having from 1 to 8 carbon atoms. Preferably R^6 is an alkyl group of 1 to 18 carbon atoms, more preferably from 1 to 10 carbon atoms, e.g. primary, secondary, and tertiary alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, t-butylethyl, t-butylpropyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, 2-ethylhexyl, decyl, dodecyl and octadecyl. Further each y preferably has a value of zero, and when n is 1, Q is preferably $-CH_2-$ or $-CHCH_3-$. Most preferably n has a value of zero. Preferred unsubstituted and substituted monovalent hydrocarbon groups represented by W include those as defined and exemplified above, for example alkyl groups having from 1 to 18 carbon atoms, preferably from 1 to 10 carbon atoms, such as primary, secondary and tertiary alkyl groups, e.g. methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, t-butylethyl, t-butylpropyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, 2-ethylhexyl, decyl and octadecyl, as well as alpha-naphthyl, beta-naphthyl, and aryl groups of the formula



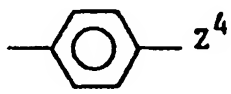
wherein X^1 and X^2 are the same as defined above, and Z^4 represents a group that may have the same meanings as X^1 and X^2, preferred alkyl groups Z^4 having from 1 to 12 carbon atoms, with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite ligand of Formula (V) above are groups having a steric hindrance of isopropyl, or more preferably t-butyl, or greater, and with the proviso that in Formula (V) above, no more than three and preferably no more than two of the X^1, X^2, Y^1 or Y^2 groups are groups having a steric hindrance of isopropyl or greater at the same time.

Among the even more preferred diorganophosphite ligands of Formula (V) above are those of the formula



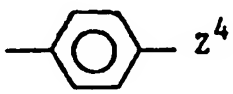
(VI)

wherein Z^2 and Z^3 each individually represent a group selected from hydroxy and $-OR^6$ wherein R^6 is an alkyl group having from 1 to 18 carbon atoms, more preferably from 1 to 10 carbon atoms, as defined above; Q represents $-CH_2-$ or $-CHCH_3-$; n has a value of 0 or 1, preferably 0; Y^1 and Y^2 each individually represent a group selected from branched chain C_3-C_{12} alkyl groups, phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl, preferably a branched chain C_3-C_5 alkyl group; and W represents a C_1-C_{18}, preferably C_1-C_{10} alkyl group, alpha-naphthyl, beta-naphthyl, and aryl groups of the formula



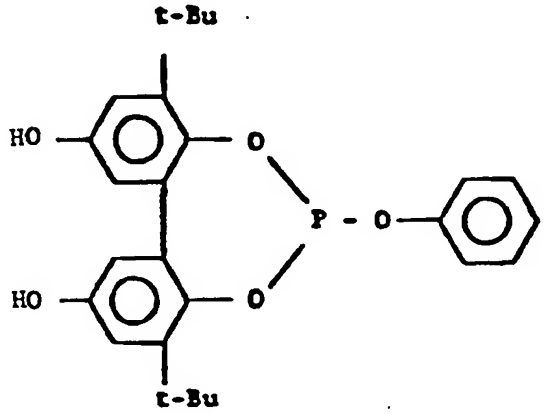
wherein Z^4 is the same as defined above.

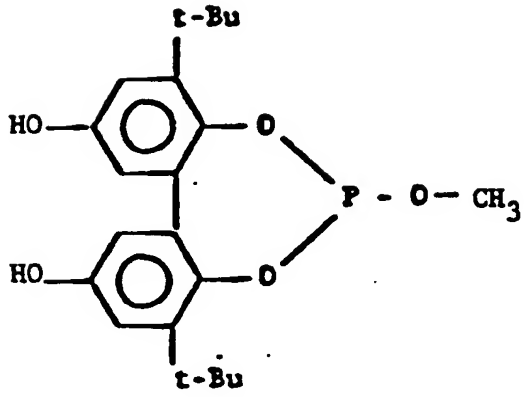
The most preferred diorganophosphite ligands represented by Formula (VI) above are those wherein Z^2 and Z^3 are hydroxy or methoxy radicals, especially methoxy, wherein Y^1 and Y^2 both represent a branched chain alkyl radical of 3 to 5 carbon atoms; especially t-butyl; wherein W is selected from C_1-C_{10} alkyl groups and aryl groups having the formula

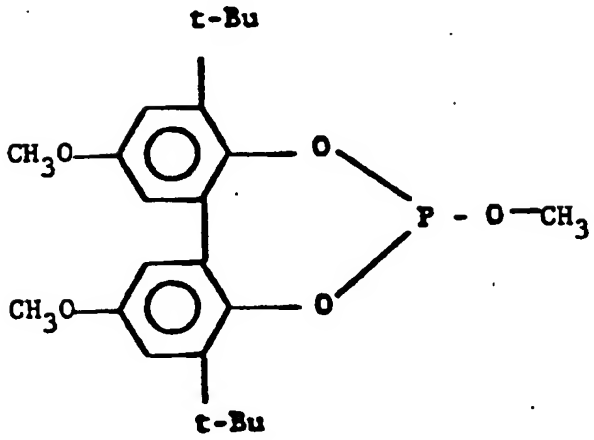


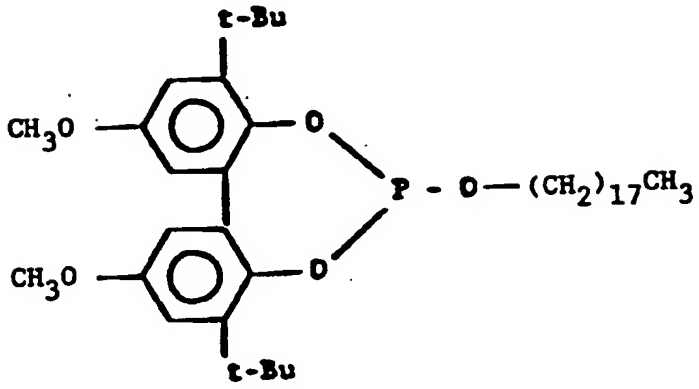
wherein Z^4 is selected from hydrogen and methoxy, especially hydrogen; and whereln Q is $-CH_2-$ or

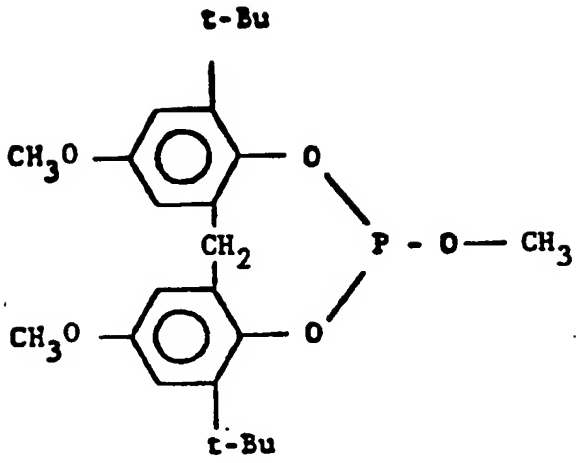
-$CHCH_3$-, n having a value of 0 or 1. More preferably W is methyl.
Illustrative examples of such diorganophosphite ligands include e.g.

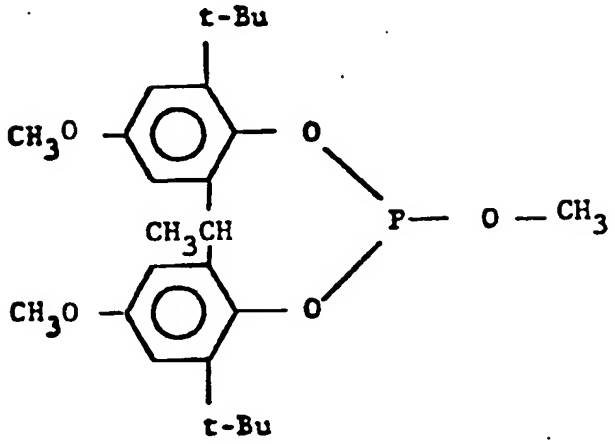


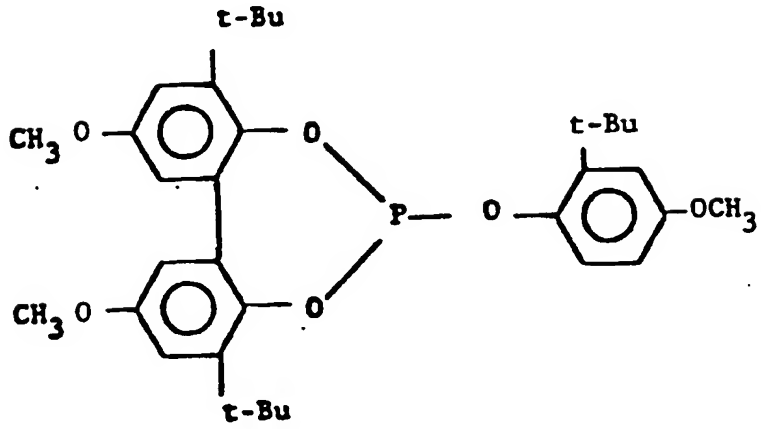

t-Bu
HO
O
P - O — CH3
HO
O
t-Bu

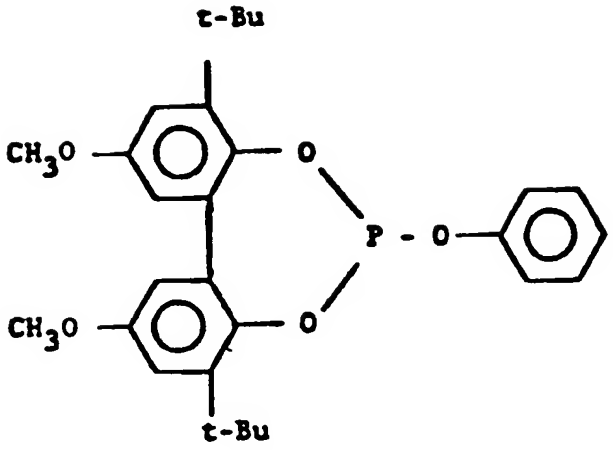

t-Bu
CH3O
O
P - O — CH3
CH3O
O
t-Bu

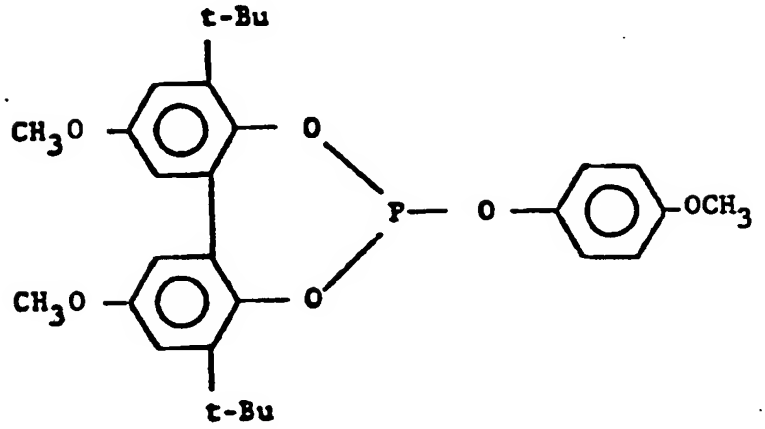

t-Bu
CH3O
O
P - O — (CH2)17CH3
CH3O
O
t-Bu

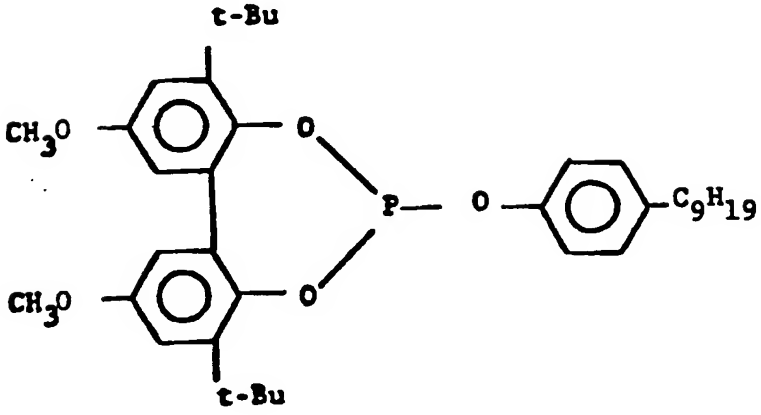

t-Bu
CH3O
O
CH2
P - O — CH3
CH3O
O
t-Bu

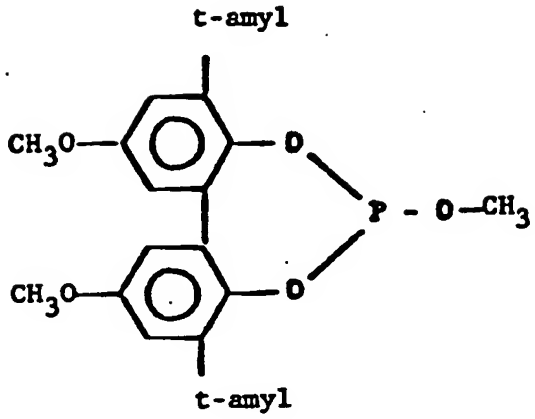

t-Bu
CH3O
O
P— O — CH3
CH3CH
CH3O
O
t-Bu

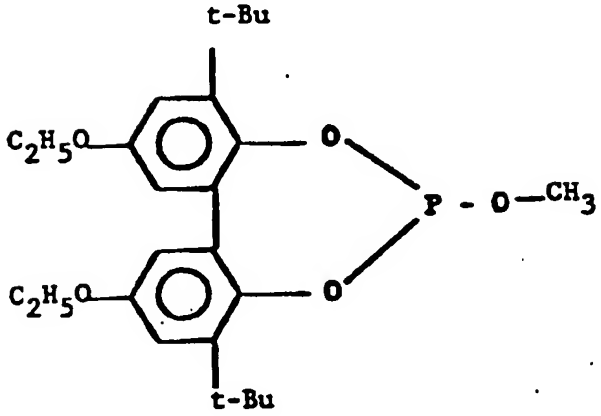

t-Bu
CH3 O
O
t-Bu
P— O
OCH3
CH3 O
O
t-Bu

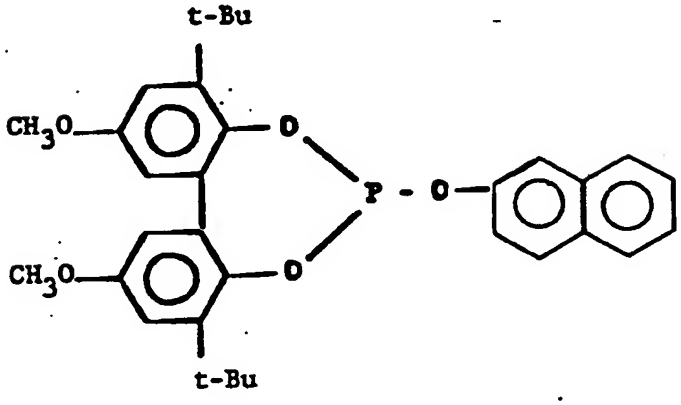

t-Bu
CH3O
O
P - O
CH3O
O
t-Bu

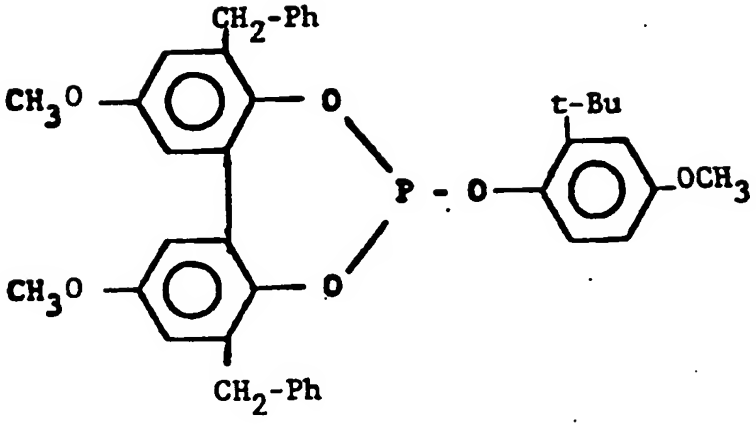

t-Bu
CH3O
O
P
O
OCH3
CH3O
O
t-Bu

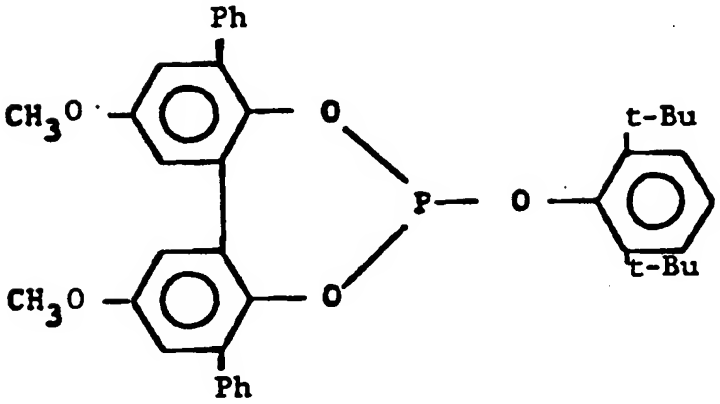

t-Bu
CH3O
O
P
O
C9H19
CH3O
O
t-Bu

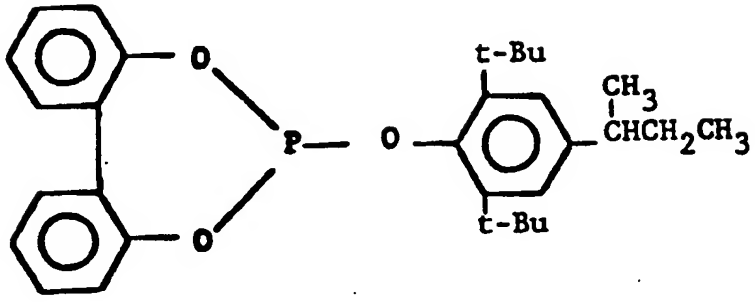

t-amyl
CH3O
O
P - O—CH3
CH3O
O
t-amyl

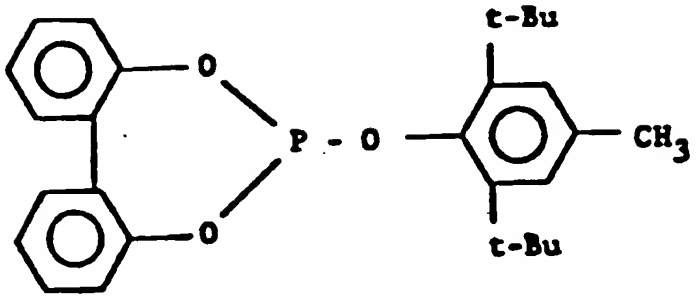

t-Bu
C2H5O
O
P - O—CH3
C2H5O
O
t-Bu

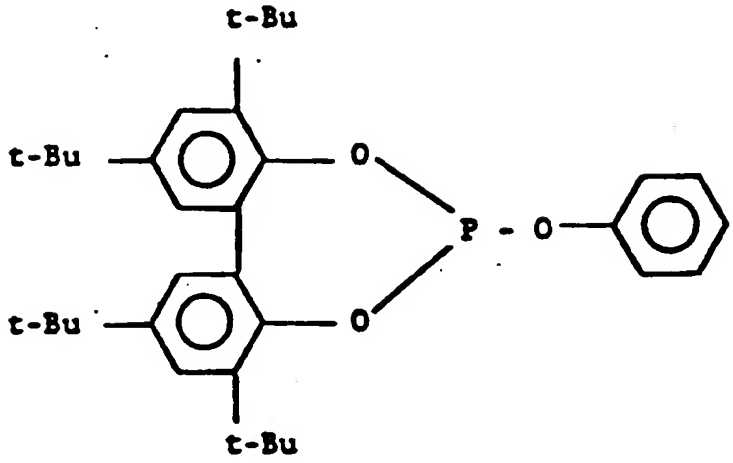

t-Bu
CH3O
O
P - O
CH3O
O
t-Bu

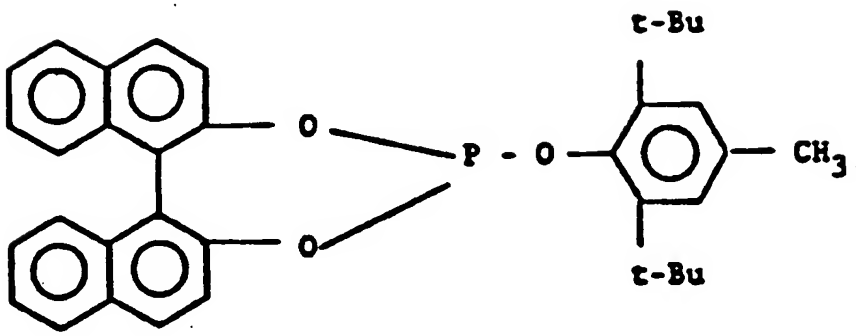


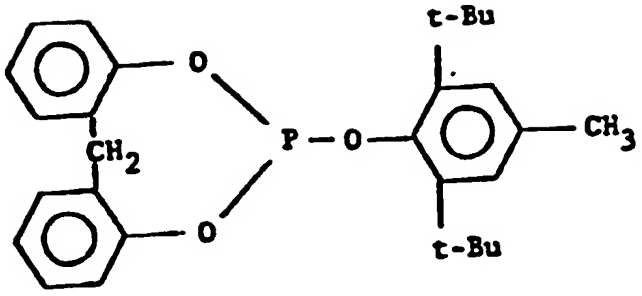


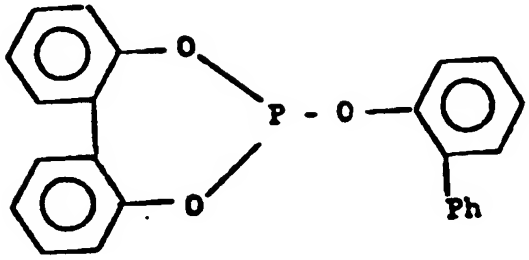


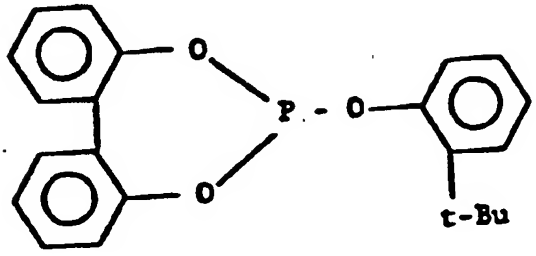

t-Bu
O
P - O
CH3
O
t-Bu

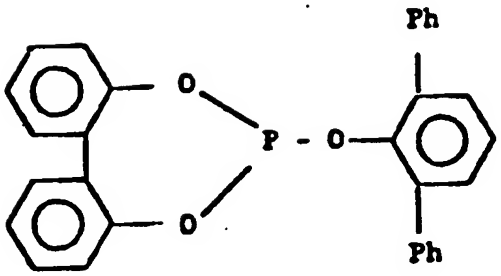

t-Bu
t-Bu
O
P - O
t-Bu
O
t-Bu

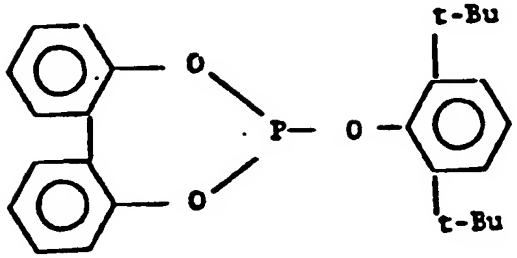

t-Bu
O
P - O
CH3
O
t-Bu

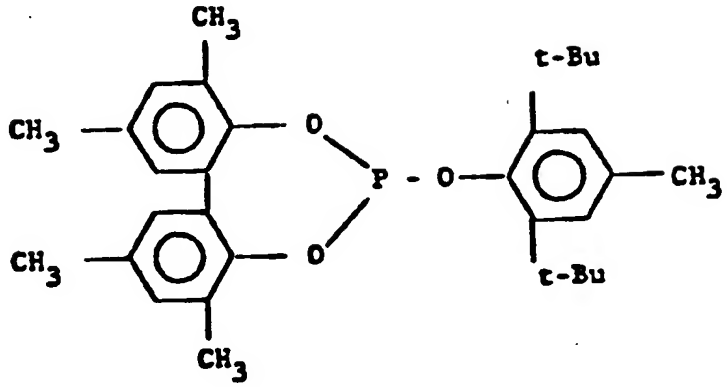

t-Bu
O
P — O
CH3
CH2
O
t-Bu

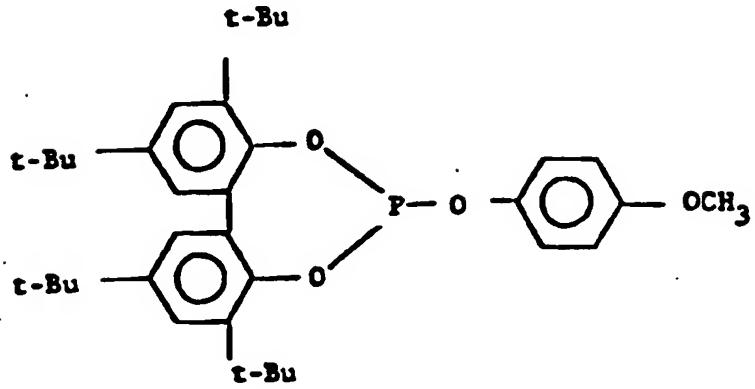

O
P - O
O
Ph

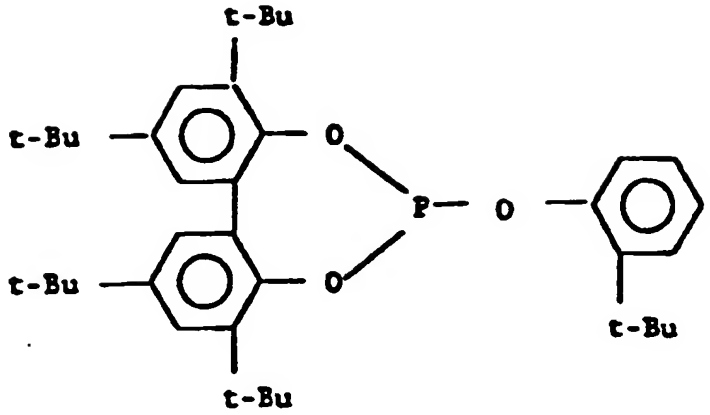

O
P - O
O
t-Bu

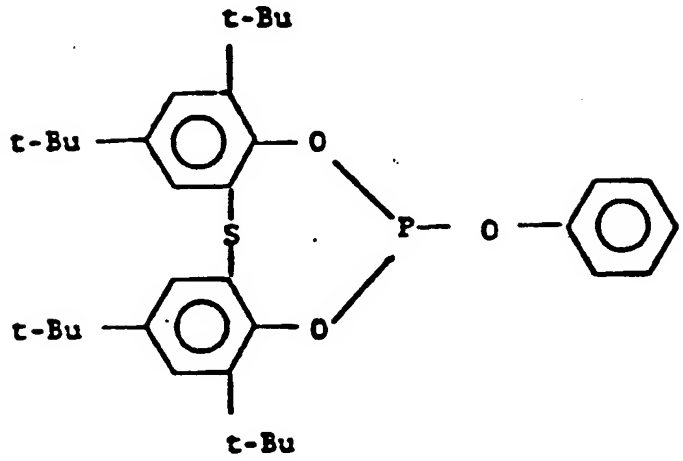

Ph
O
P - O
O
Ph

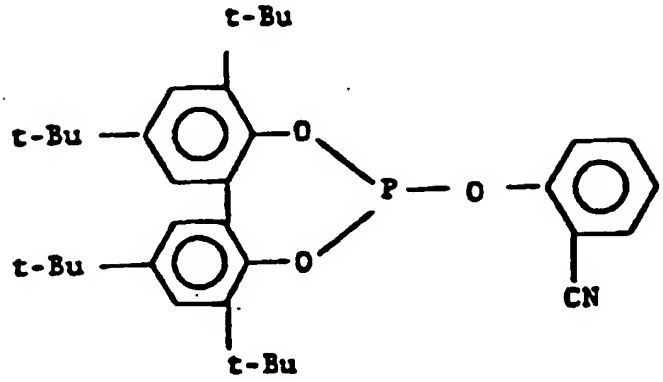

t-Bu
O
P— O
O
t-Bu

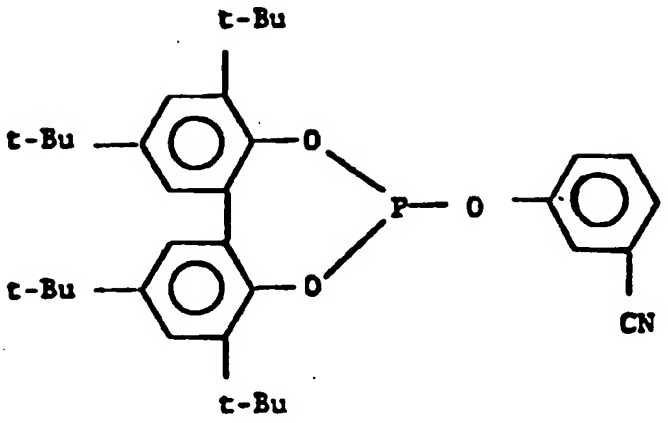

CH3
t-Bu
CH3
O
P - O
CH3
CH3
O
t-Bu
CH3

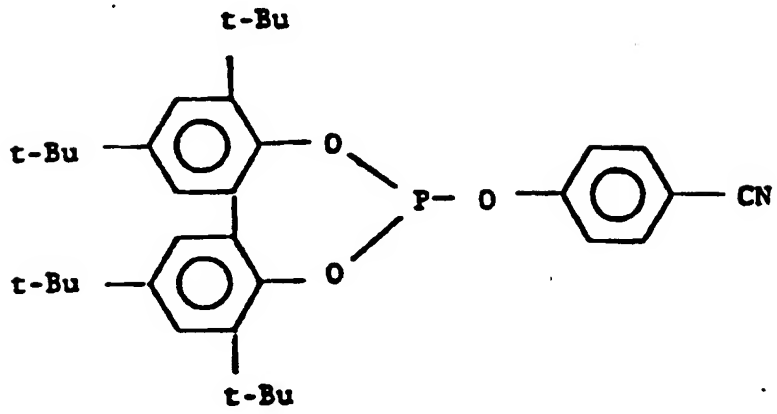

t-Bu
t-Bu
O
P— O
OCH3
t-Bu
O
t-Bu

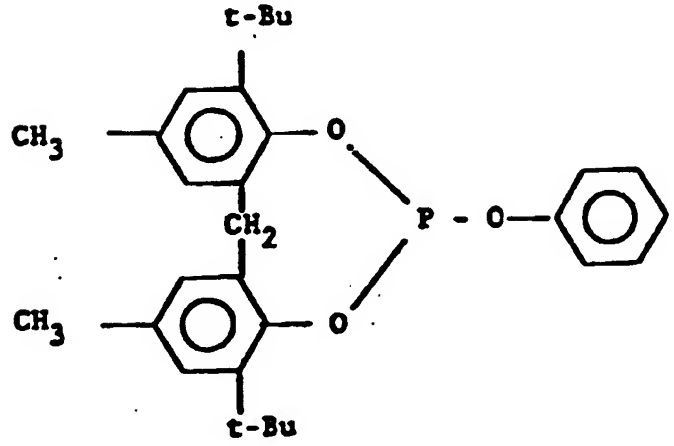

t-Bu
t-Bu
O
P
O
t-Bu
t-Bu
O
t-Bu
t-Bu

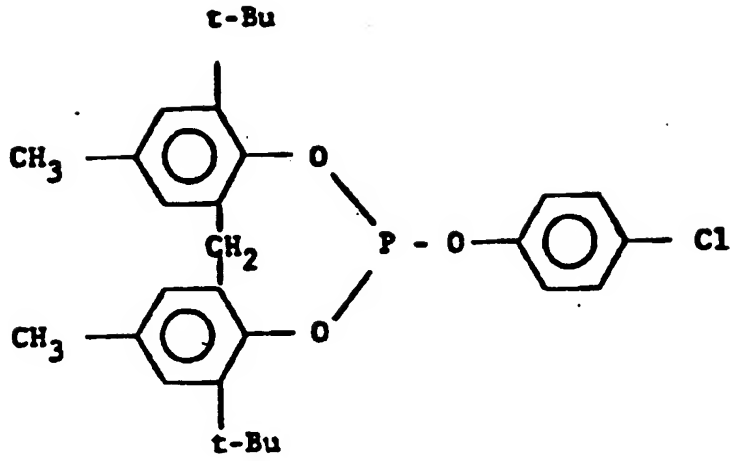

t-Bu
t-Bu
O
S
P
O
t-Bu
O
t-Bu
t-Bu

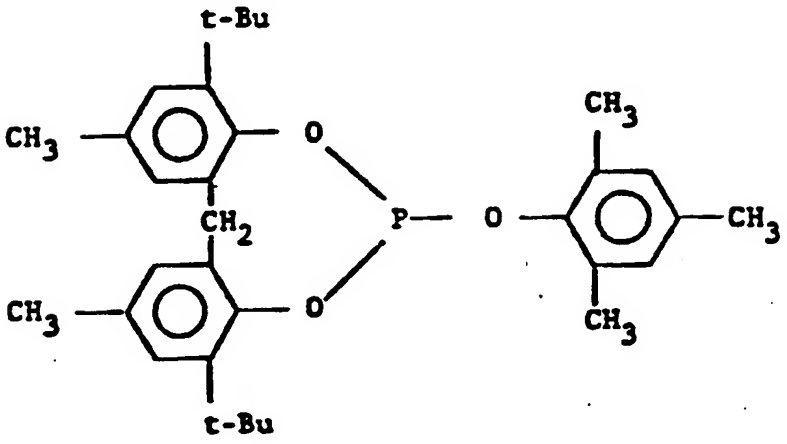

t-Bu
t-Bu
O
P
O
CN
t-Bu
O
t-Bu
t-Bu

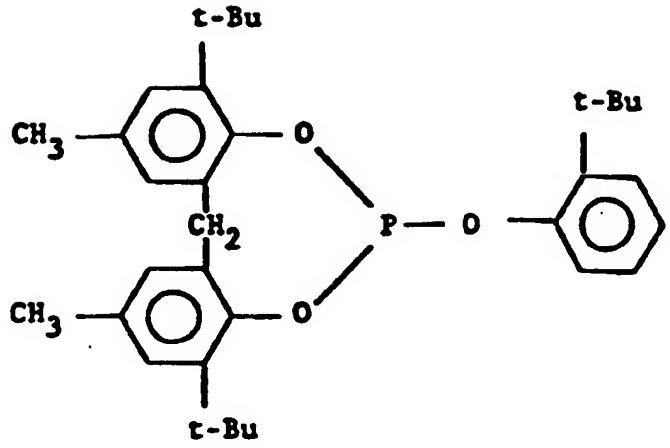

t-Bu
t-Bu
O
P
O
t-Bu
O
CN
t-Bu

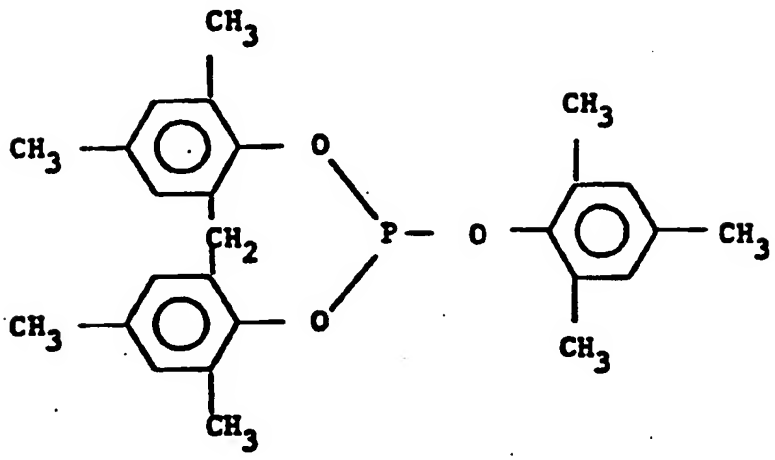

t-Bu
t-Bu
O
P
O
CN
t-Bu
O
t-Bu

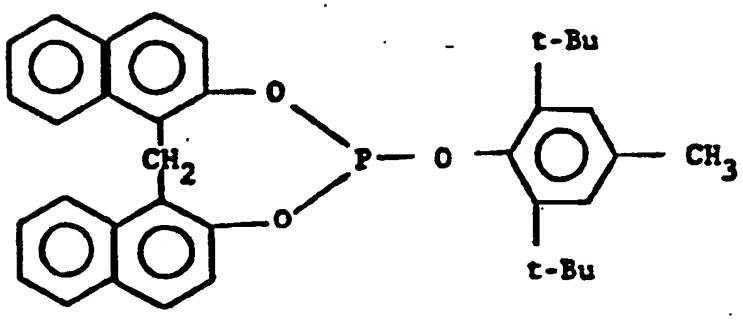

t-Bu
CH3
O
P
O
CH2
CH3
O
t-Bu

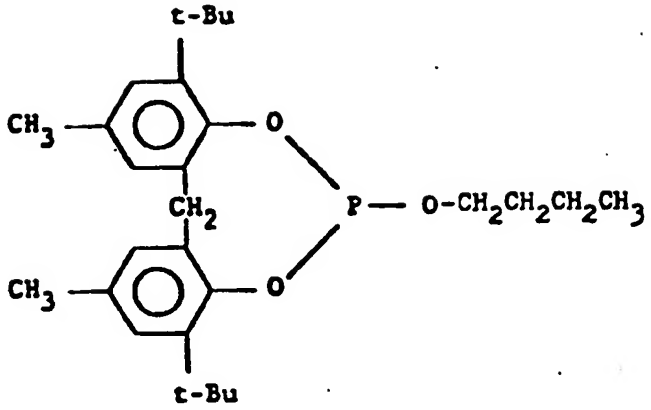

t-Bu
CH3
O
CH2
P - O
Cl
CH3
O
t-Bu

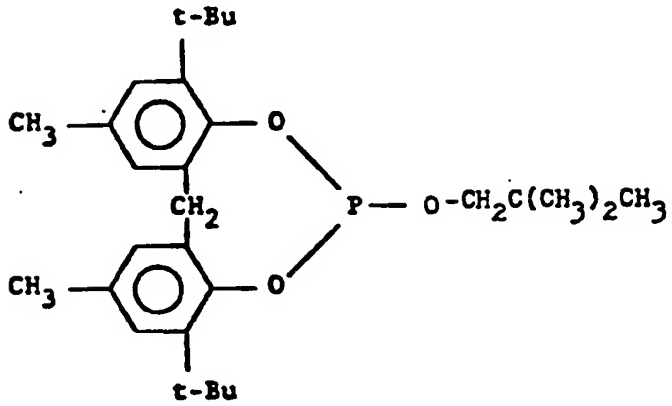

t-Bu
CH3
O
CH3
CH2
P
O
CH3
CH3
O
CH3
t-Bu

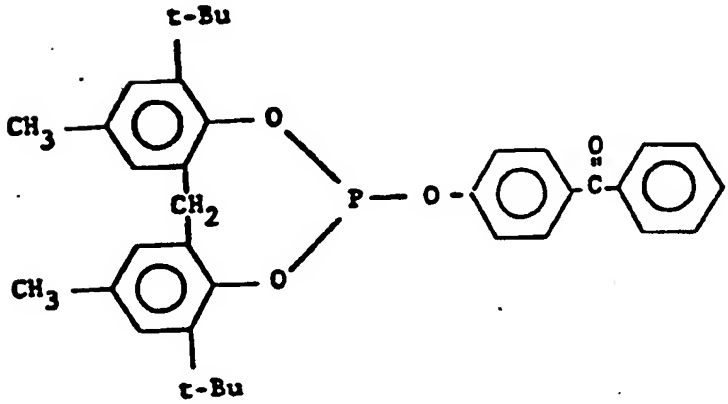

t-Bu
CH3
O
t-Bu
CH2
P
O
CH3
O
t-Bu

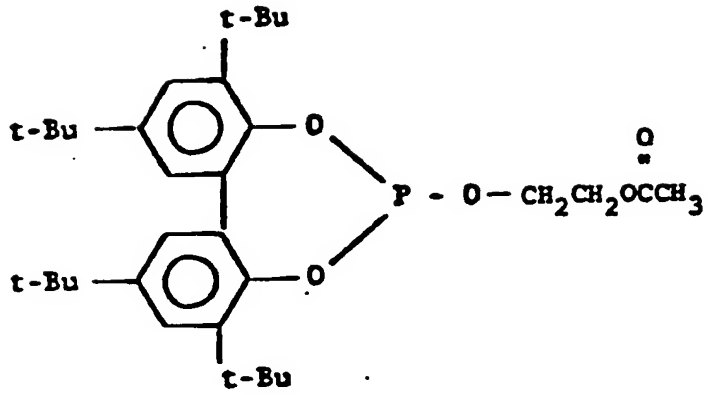

CH3
CH3
O
CH3
CH2
P
O
CH3
CH3
O
CH3

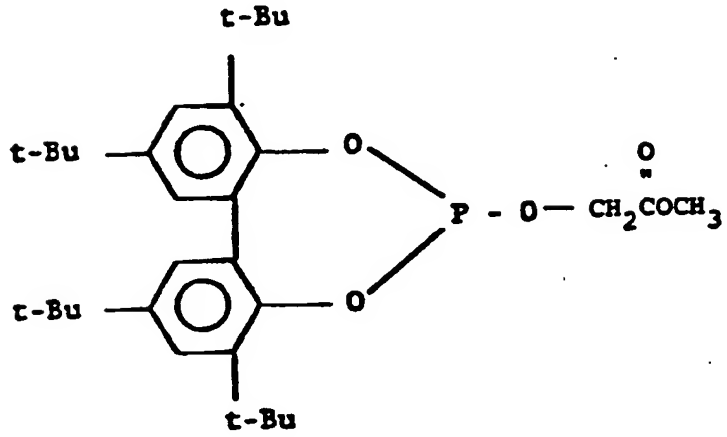

O
t-Bu
CH2
P
O
CH3
O
t-Bu

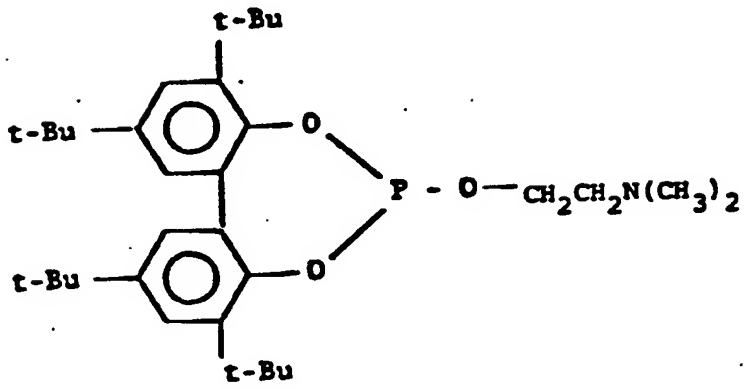


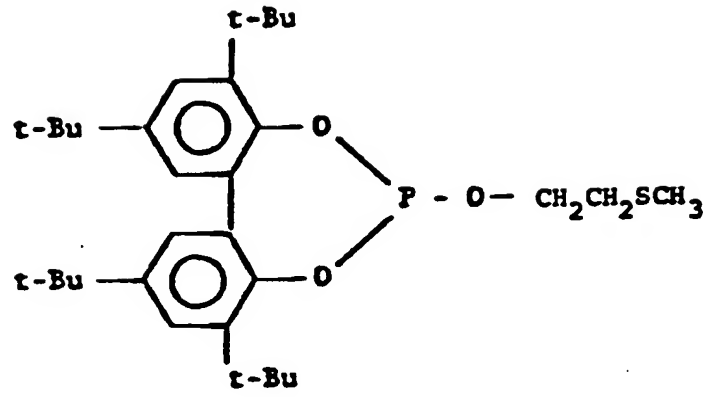


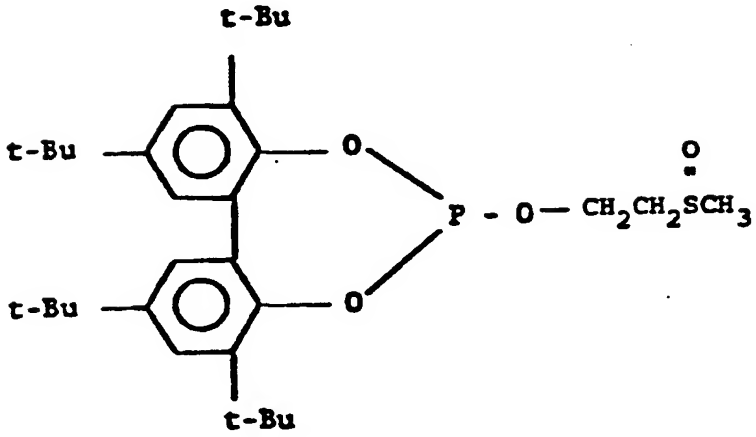


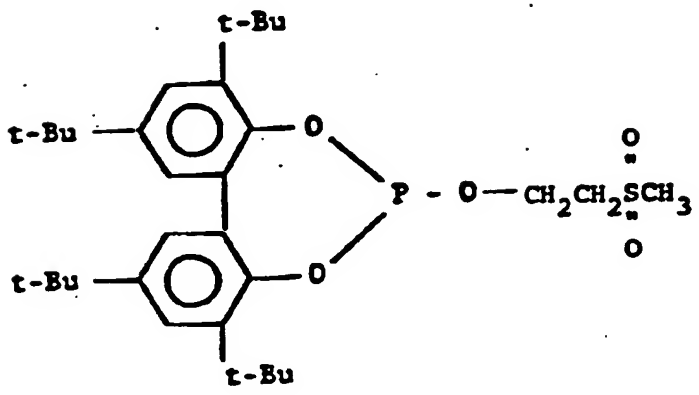


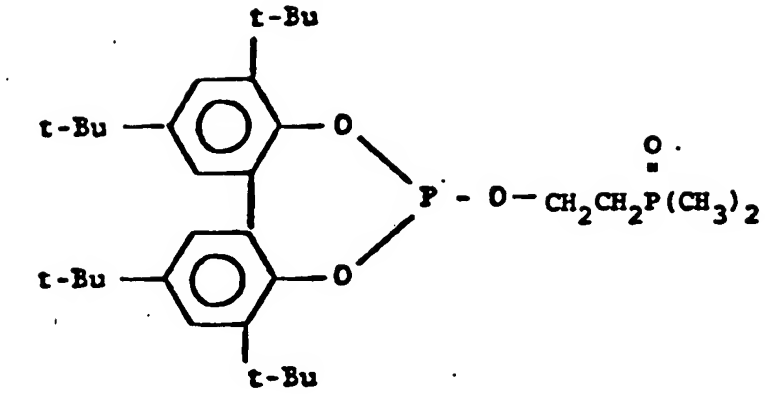


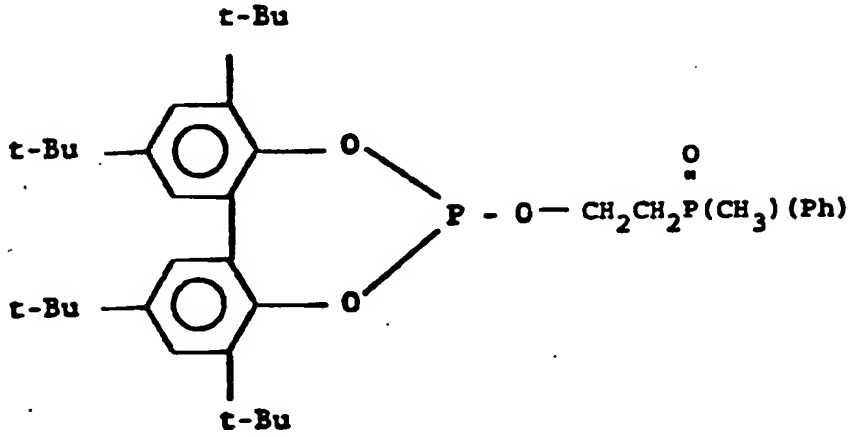


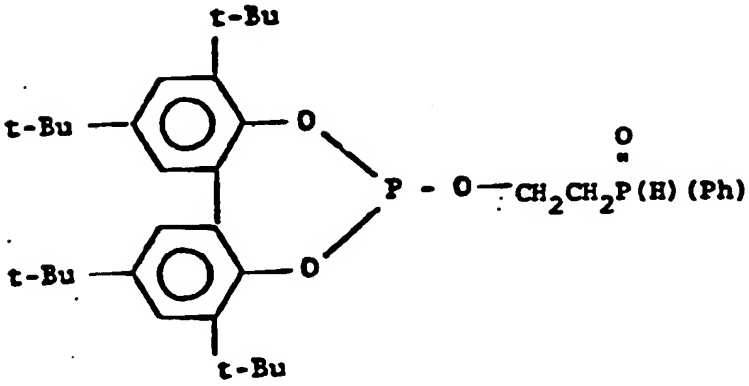


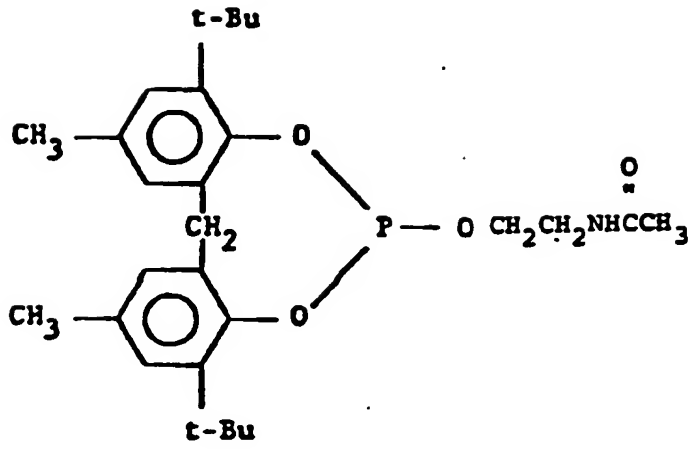








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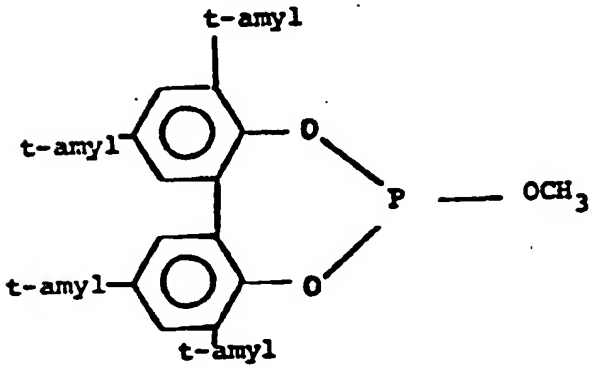
CH3
O
CH2
P
O CH2CH2NHCCH3
O
CH3
O
t-Bu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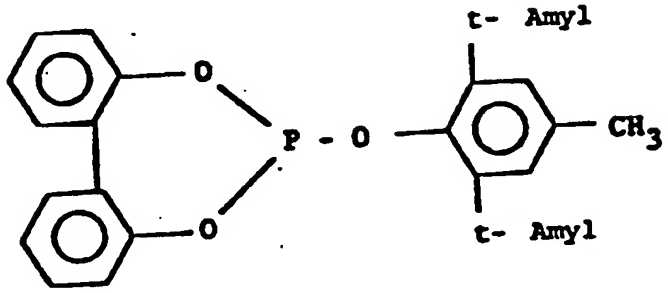
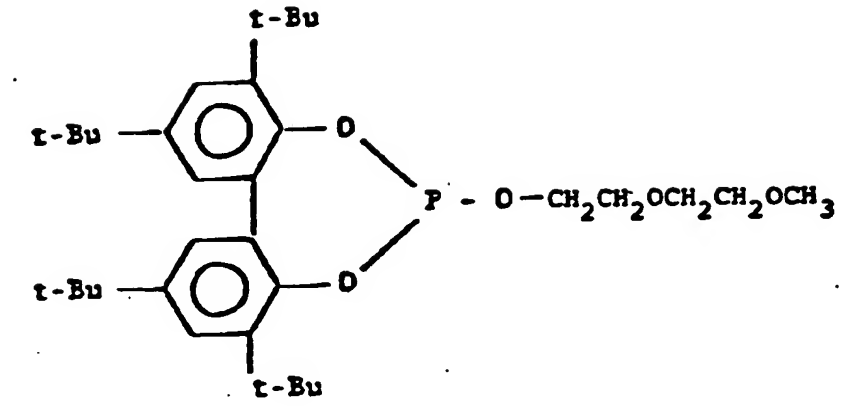
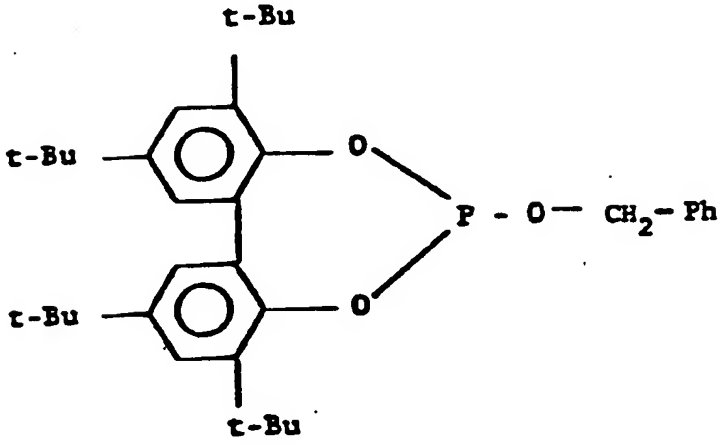
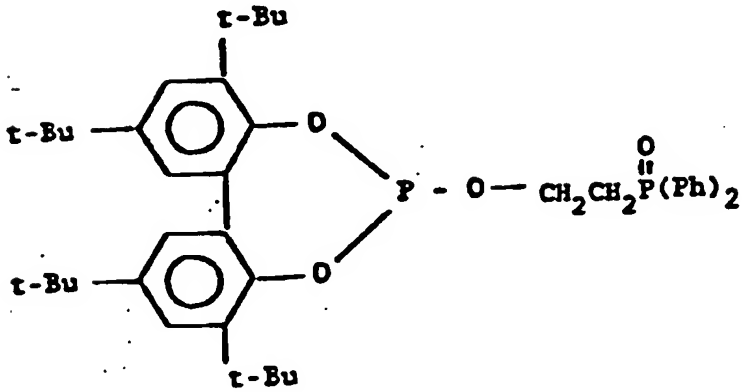
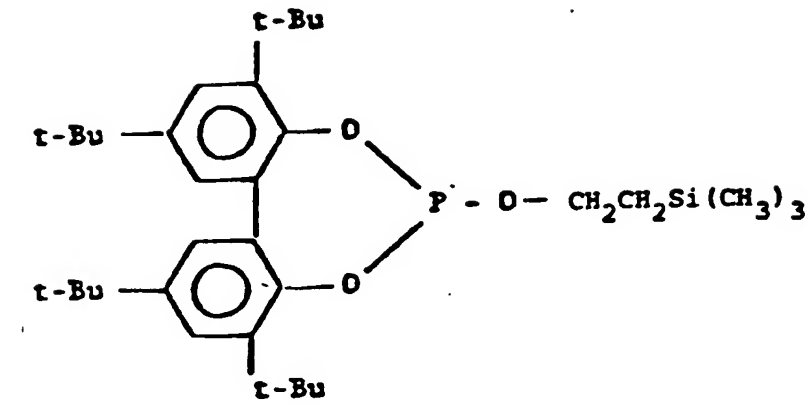
t-amyl
O
P
OCH3
t-amyl
O
t-amyl

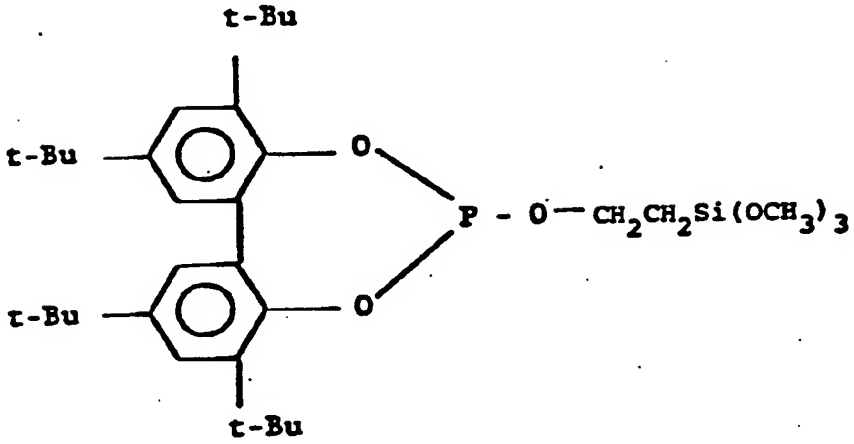

t- Amyl
O
P - O
CH3
O
t- Amyl

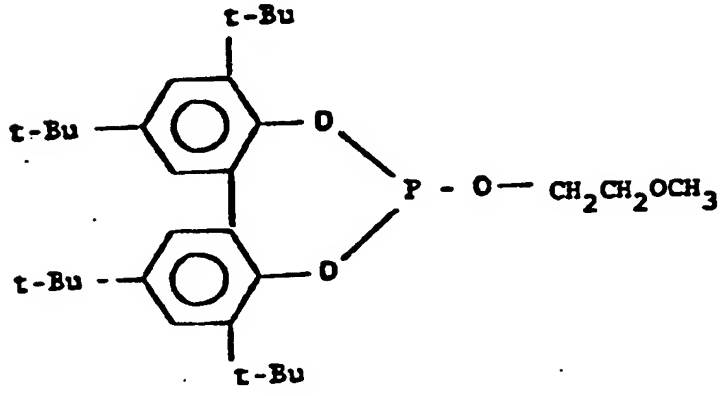

t-Bu
t-Bu
O
P - O—CH2CH2OCH2CH2OCH3
t-Bu
O
t-Bu


t-Bu
t-Bu
O
P - O— CH2— Ph
t-Bu
O
t-Bu

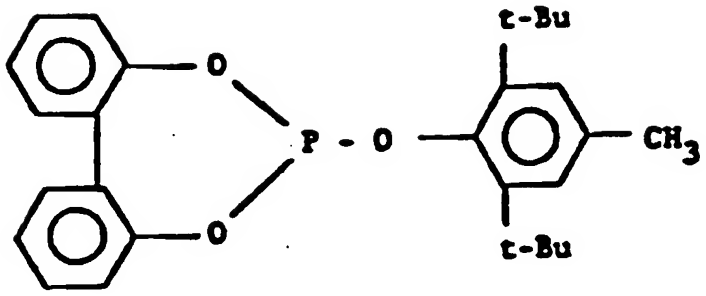

t-Bu
t-Bu
O
O
P - O— CH2CH2P(Ph)2
t-Bu
O
t-Bu



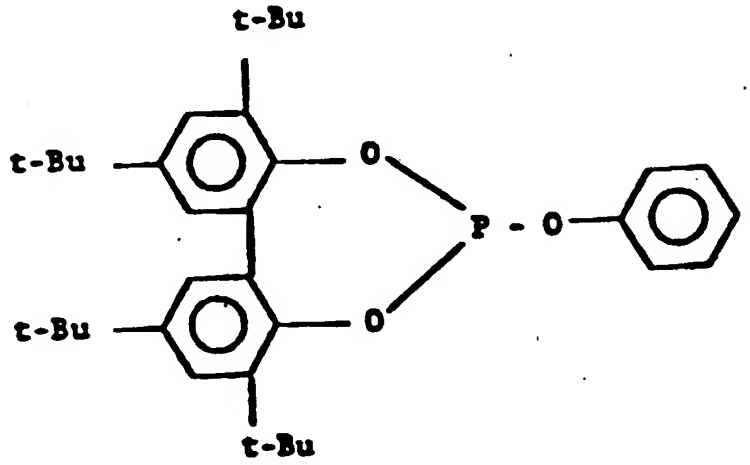




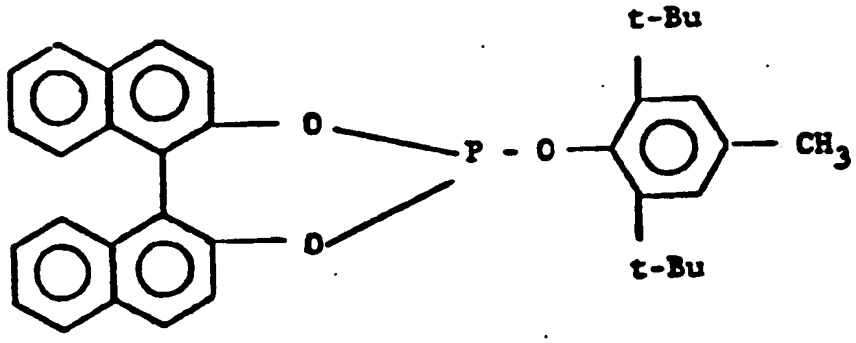
In the above diorganophosphite formulas t-Bu represents a tertiary butyl radical, Ph represents a phenyl ($-C_6H_5$) radical and ($-C_9H_{19}$) represents branched mixed nonyl radicals. The most preferred diorganophosphite ligands employable in this invention are those of the formulas



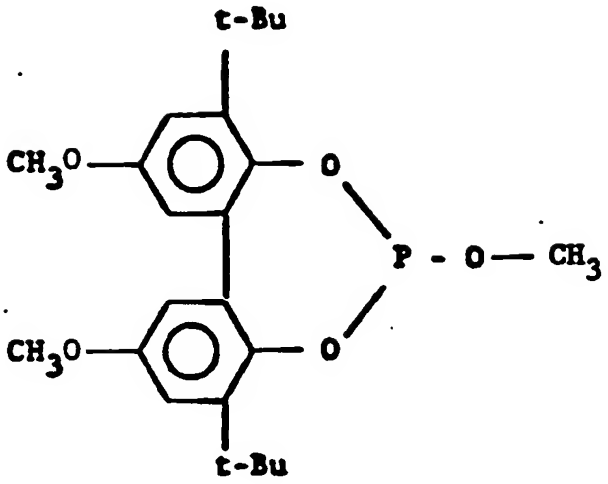
1,1'-biphenyl-2,2'-diyl-(2,6-di-t-butyl-4-methylphenyl)phosphite



phenyl [3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl] phosphite



1,1'-binaphthylene-2,2'-diyl-(2,6 di-t-butyl-4-methylphenyl)phosphite



methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite

As noted above the diorganophosphite ligands defined above are employed in this invention as both the phosphorus ligand of the rhodium complex catalyst as well as the free phosphorus ligand that is present in the reaction medium of the process of this invention. In addition, it is to be understood that while the phosphorus ligand of the rhodium-diorganophosphite complex catalyst and excess free phosphorus ligand present in the process of this invention are normally the same type of diorganophosphite ligand, different types of diorganophosphite ligands as well as mixtures of two or more different diorganophosphite ligands may be employed for each purpose in said process, if desired.

As in the case of prior art Group VIII transition metal-phosphorus complex catalysts, the rhodium-diorganophosphite complex catalysts of this invention may be formed by methods known in the art. For instance, preformed rhodium hydridocarbonyl (diorganophosphite) catalysts may possibly be prepared and introduced into the reaction medium of the hydroformylation process. More preferably, the rhodium-diorganophosphite complex catalysts of this invention can be derived from a metal catalyst precursor which may be introduced into the reaction medium for in situ formation of the active catalyst. For example, rhodium catalyst precursors such as rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$ and the like may be introduced into the reaction medium along with the diorganophosphite ligand for the in situ formation of the active catalyst. In a preferred embodiment rhodium dicarbonyl acetylacetonate is employed as a rhodium precursor and reacted in the presence of a solvent with the diorganophosphite to form a catalytic rhodium carbonyl diorganophosphite acetylacetonate precursor which is introduced into the reactor along with excess free diorganophosphite ligand for the in situ formation of the active catalyst. In any event, it is sufficient for the purpose of this invention to understand that carbon monoxide, hydrogen and diorganophosphite are all ligands that are capable of being complexed with the rhodium and that an active rhodium-diorganophosphite catalyst is present in the reaction medium under the conditions of the hydroformylation process.

Accordingly, the rhodium-diorganophosphite complex catalysts of this invention may be defined as consisting essentially of rhodium complexed with carbon monoxide and a diorganophosphite ligand. Of course, it is to be understood that the catalyst terminology "consisting essentially of" is not meant to exclude, but rather include hydrogen complexed with the rhodium, in addition to carbon monoxide and the diorganophosphite ligand. Moreover, as noted above such terminology is also not meant to exclude the possibility of other organic ligands and/or anions that might also be complexed with the rhodium. However, such catalyst terminology preferably is meant to exclude other materials in amounts which unduly adversely poison or unduly deactivate the catalyst and thus rhodium most desirably is free of contaminants such as rhodium bound halogen e.g. chlorine, and the like. As noted, the hydrogen and/or carbonyl ligands of an active rhodium-diorganophosphite complex catalyst may be present as a result of being ligands bound to a precursor catalyst and/or as a result of in-situ formation e.g. due to the hydrogen and carbon monoxide gases employed in a hydroformylation process.

Moreover, like prior art Group VIII transition metal phosphorus ligand complex catalysts it is clear that the amount of complex catalyst present in the reaction medium of the hydroformylation process of this invention need only be that minimum amount necessary to provide the given rhodium concentration desired

to be employed and which will furnish the basis for at least that catalytic amount of rhodium necessary to catalyze the hydroformylation process. Moreover, one of the benefits of this invention is the generally improved catalytic activity obtainable by the use of the diorganophosphite ligands employable herein. Such improved catalytic activity can translate into a considerable processing asset, particularly since a rare and expensive metal (rhodium) is to be employed, since lower reaction temperatures and/or lower amounts of catalytically active metal may be employed to achieve a desired rate of productivity than may be possible when less active catalysts are employed. In general, rhodium concentrations in the range of from about 10 ppm to about 1000 ppm, calculated as free metal, should be sufficient for most hydroformylation processes. Moreover, it is generally preferred to employ from about 10 to 500 ppm of rhodium and more preferably from 25 to 350 ppm of rhodium, calculated as free metal.

The olefinic starting material reactants encompassed by the process of this invention can be terminally or internally unsaturated and be of straight-chain, branched-chain or cyclic structure. Such olefins can contain from 2 to 20 carbon atoms and may contain one or more ethylenic unsaturated groups. Moreover, such olefins may contain groups or substituents which do not essentially adversely interfere with the hydroformylation process such as carbonyl, carbonyloxy, oxy, hydroxy, oxycarbonyl, halogen, alkoxy, aryl, haloalkyl, and the like. Illustrative olefinic unsaturated compounds include alpha olefins, internal olefins, alkyl alkenoates, alkenyl alkanoates, alkenyl alkyl ethers, alkenols, and the like, e.g. ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-octadecene, 2-butene, 2-methyl propene (isobutylene), isoamylene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, cyclohexene, propylene dimers, propylene trimers, propylene tetramers, 2-ethyl-1-hexene, styrene, 3-phenyl-1-propene, 1,4-hexadiene, 1,7 octadiene, 3-cyclohexyl-1-butene, allyl alcohol, hex-1-en-4-ol, oct-1-en-4-ol, vinyl acetate, allyl acetate, 3-butenyl acetate, vinyl propionate, allyl propionate, allyl butyrate, methyl methacrylate, 3-butenyl acetate, vinyl ethyl ether, vinyl methyl ether, allyl ethyl ether, n-propyl-7-octenoate, 3-butenenitrile, 5-hexenamide, and the like. Of course, it is understood that mixtures of different olefinic starting materials can be employed, if desired, by the hydroformylation process of the subject invention. More preferably the subject invention is especially useful for the production of aldehydes, by hydroformylating alpha olefins containing from 2 to 20 carbon atoms and internal olefins containing from 4 to 20 carbon atoms as well as starting material mixtures of such alpha olefins and internal olefins. The most preferred olefin starting materials are butene-1, butene-2 (cis and/or trans), isobutene and various mixtures thereof.

The hydroformylation process of this invention is also preferably conducted in the presence of an organic solvent for the rhodium-diorganophosphite complex catalyst. Any suitable solvent which does not unduly adversely interfere with the hydroformylation process can be employed and such solvents may include those heretofore commonly employed in known Group VIII transition metal catalyzed processes. By way of illustration suitable solvents for rhodium catalyzed hydroformylation processes include those disclosed e.g. in 3,527,809 and 4,148,830. Of course, mixtures of one more different solvents may be employed if desired. In general, in rhodium catalyzed hydroformylation it is preferred to employ aldehyde compounds corresponding to the aldehyde products desired to be produced and/or higher boiling aldehyde liquid condensation by-products as the primary solvent such as the higher boiling aldehyde liquid condensation by-products that are produced in situ during the hydroformylation process. Indeed, while one may employ, if desired, any suitable solvent at the start up of a continuous process (aldehyde compounds corresponding to the desired aldehyde products being preferred), the primary solvent will normally eventually comprise both aldehyde products and higher boiling aldehyde liquid condensation by-products due to the nature of such continuous processes. Such aldehyde condensation by-products can also be preformed if desired and used accordingly. Moreover, such higher boiling aldehyde condensation by-products and methods for their preparation are more fully described in US-A-4,148,830 and 4,247,486. Of course, it is obvious that the amount of solvent employed is not critical to the subject invention and need only be that amount sufficient to provide the reaction medium with the particular rhodium concentration desired. In general, the amount of solvent when employed may range from about 5 percent by weight up to about 95 percent by weight or more based on the total weight of the reaction medium.

It is further generally preferred to carry out the hydroformylation process of this invention in a continuous manner. Such types of continuous processes are well known in the art and may involve e.g. hydroformylating the olefinic starting material with carbon monoxide and hydrogen in a liquid homogeneous reaction medium comprising a solvent, the rhodium-diorganophosphite catalyst, and free diorganophosphite ligand; supplying make-up quantities of the olefinic starting material, carbon monoxide and hydrogen to the reaction medium; maintaining reaction temperature and pressure conditions favorable to the hydroformylation of the olefinic starting material; and recovering the desired aldehyde hydroformylation product in any conventional manner desired. While the continuous process can be carried out in a single pass mode, i.e. wherein a vaporous mixture comprising unreacted olefinic starting material and vaporized aldehyde

product is removed from the liquid reaction medium from whence the aldehyde product is recovered and make-up olefinic starting material, carbon monoxide and hydrogen are supplied to the liquid reaction medium for the next single pass through without recycling the unreacted olefinic starting material, it is generally desirable to employ a continuous process that involves either a liquid and/or gas recycle procedure. Such types of recycle procedures are well known in the art and may involve the liquid recycling of the rhodium-diorganophosphite complex catalyst solution separated from the desired aldehyde reaction product, such as disclosed e.g. in US-A-4,148,830 or a gas recycle procedure such as disclosed e.g. in US-A-4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The most preferred hydroformylation process of this invention comprises a continuous liquid catalyst recycle process.

The desired aldehyde product may be recovered in any conventional manner such as described, e.g. in US-A-4,148,830 and 4,247,486. For instance, in a continuous liquid catalyst recycle process the portion of the liquid reaction solution (containing aldehyde product, catalyst, etc.) removed from the reactor can be passed to a vaporizer/separator wherein the desired aldehyde product can be separated via distillation, in one or more stages, under normal, reduced or elevated pressure,from the liquid reaction solution, condensed and collected in a product receiver, and further purified if desired. The remaining non-volatilized catalyst containing liquid reaction solution may then be recycled back to the reactor as may if desired any other volatile materials, e.g. unreacted olefin, together with any hydrogen and carbon monoxide dissolved in the liquid reaction solution after separation thereof from the condensed aldehyde product, e.g. by distillation in any conventional manner. In general, it is preferred to separate the desired aldehyde product from the rhodium catalyst containing product solution under reduced pressure and at low temperatures such as below 150 °C. and more preferably below 130 °C.

As noted above, the hydroformylation process of this invention is carried out in the presence of free diorganophosphite ligand, i.e. ligand that is not complexed with the rhodium of the metal complex catalyst employed. Thus the free diorganophosphite ligand may correspond to any of the above defined diorganophosphite ligands discussed above. However, while it is preferred to employ a free diorganophosphite ligand that is the same as the diorganophosphite ligand of the rhodium-diorganophosphite complex catalyst such ligands need not be the same in a given process, but can be different if desired. While the hydroformylation process of this invention may be carried out with any excess amount of free diorganophosphite ligand desired, e.g. at least one mole of free diorganophosphite ligand per mole of rhodium present in the reaction medium, it has been found that in rhodium catalyzed hydroformylation large amounts of free diorganophosphite ligand are not necessary for catalytic activity and/or catalyst stabilization, and generally retard the activity of the rhodium catalyst. Accordingly, in general amounts of diorganophosphite ligand of from about 4 to about 50, and preferably from about 6 to about 25, moles per mole of rhodium present in the reaction medium should be suitable for most purposes, said amounts of diorganophosphite ligand employed being the sum of both the amount of diorganophosphite that is bound (complexed) to the rhodium present and the amount of free (non-complexed) diorganophosphite ligand present. Of course, if desired, make-up diorganophosphite ligand can be supplied to the reaction medium of the hydroformylation process, at any time and in any suitable manner, to maintain a predetermined level of free ligand in the reaction medium.

The ability to carry out the process of this invention in the presence of free diorganophosphite ligand is an important beneficial aspect of this invention in that it removes the criticality of employing very low precise concentrations of ligand that may be required of certain complex catalysts whose activity may be retarded when even any amount of free ligand is also present during the process, particularly when large scale commercial operations are involved, thus helping to provide the operator with greater processing latitude.

The reaction conditions for effecting a hydroformylation process of this invention may be those heretofore conventionally used and may comprise a reaction temperature of from about 45 °C to about 200 °C and pressures ranging from about 6,9 kPa to about 69 MPa (about 1 to 10,000 psia).

While it may be possible to produce aldehyde products having a high normal (straight chain) to branched chain aldehyde product ratio, e.g. on the order of about 5 to 1 or greater, by the hydroformylation process of this invention, in general the preferred hydroformylation will be that process which is most efficient in producing aldehyde product rich in branched chain aldehyde, i.e. aldehyde product having a low normal (straight chain) aldehyde to branched chain aldehyde product ratio, e.g. on the order of 5 moles or less of n-aldehyde product to 1 mole of branched aldehyde product. Moreover, a unique feature of the present invention is the overall processing latitude afforded in controlling the aldehyde product selectivity that is provided by the use of the diorganophosphite ligands employable herein. For instance, due to isomerization of the olefin starting material during hydroformylation that occurs with the use of the diorganophosphite ligands employable herein, one may control or preselect the particular richness of

branched aldehyde in the product desired (i.e. preselect the particular desired ratio of normal to branched aldehyde product), which is in marked contrast to hydroformylations that employ phosphorus ligands which show little or no ability to permit isomerization of the olefin starting material during such reactions leaving one with little or no ability to control the ratio of normal to branched chain aldehyde product that may be desired.

For example, alpha-olefins such as butene-1 may be readily hydroformylated by the process of this invention to produce aldehyde products having straight chain to branched chain aldehyde product ratios of less than 5 to 1, preferably less than 3 to 1 and more preferably about 2 to 1. On the other hand internal olefins may be surprisingly hydroformylated by the process of this invention to obtain aldehyde products that are even richer in their branched chain isomers. For instance pure butene-2 can be hydroformylated to obtain more 2-methyl-butyraldehyde, i.e. aldehyde products wherein the ratio of n-valeraldehyde to 2-methylbutyraldehyde is about 2 to 1 or less, preferably less than 1 to 1 and more preferably less than 0.5 to 1. Such processing latitude of the present invention, provided in part by isomerization of the olefin starting material during hydroformylation and the choice of the diorganophosphite ligand employed, is especially useful in those instances when a particular optimization of the branched chain aldehyde product is desirable. For instance, since 2-methylbutyraldehyde is the precursor of isoprene which is used to produce synthetic rubber, the ability to produce essentially only 2-methylbutyraldehyde directly by the hydroformylation process of this invention is extremely beneficial to the art in that it greatly facilitates the refining operation (separation from n-valeraldehyde) and allows for the production of higher amounts of desired 2-methylbutyraldehyde product per given amount of butene-2 starting material. On the other hand, there are clearly instances when it may be desirable that the aldehyde product need not be quite so rich in branched chain aldehyde, but may comprise a slightly higher normal to branched chain aldehyde product ratio such as when the aldehydes are employed as precursors for alcohols and acids which in turn may find utility in such diverse fields as synthetic lubricants, solvents, paints, fertilizers, and the like.

Likewise mixtures of alpha-olefins and internal olefins can also be readily hydroformylated by the process of this invention to obtain aldehyde products that are rich in their branched chain isomers. For instance starting material mixtures of butene-1 and butene-2 can readily be hydroformylated to obtain aldehyde products wherein the ratio of straight chain aldehyde to branched chain aldehyde is about 3 to 1 or less and more preferably about 2 to 1 or less. The ability to hydroformylate both types of olefins concurrently with comparable facility from the same starting material mixture is highly beneficial to the art since such mixed alpha olefin and internal olefin starting materials are readily available and are the most economical olefin feedstocks. Moreover, the versatility of the diorganophosphite ligands employable herein lend themselves readily to the continuous hydroformylation of both alpha-olefins and internal olefins wherein different reactors in series may be employed. Such ability not only provides one with the processing latitude of further hydroformylating in the second reactor any unreacted olefin passed to it from the first reactor but also allows one, if desired, to optimize the reaction conditions for hydroformylation of e.g. the alpha-olefin in the first reactor , while also optimizing the reaction conditions for the hydroformylation of e.g. the internal olefin in the second reactor.

Of course, it is to be understood that while the optimization of the reaction conditions necessary to achieve the best results and efficiency desired are dependent upon one's experience in the utilization of the subject hydroformylation invention, only a certain measure of experimentation should be necessary to ascertain those conditions which are optimum for a given situation and such should be well within the knowledge of one skilled in the art and easily obtainable by following the more preferred aspects of this invention as explained herein and/or by simple routine experimentation.

For instance, the total gas pressure of hydrogen, carbon monoxide and olefinic unsaturated starting compound of the hydroformylation process of this invention may range from about 6,9 kPa to about 69 MPa (about 1 to about 10,000 psi). More preferably, however, in the hydroformylation of olefins to produce aldehydes it is preferred that the process be operated at a total gas pressure of hydrogen, carbon monoxide and olefinic unsaturated starting compound of less than about 10340 kPa (1500 psia.) and more preferably less than about 3450 kPa (500 psia.). The minimum total pressure of the reactants is not particularly critical and is limited predominately only by the amount of reactants necessary to obtain a desired rate of reaction. More specifically the carbon monoxide partial pressure of the hydroformylation process of this invention is preferably from about 6,9 to about 828 kPa (about 1 to about 120 psia.) and more preferably from about 21 to about 620 kPa (about 3 to about 90 psia), while the hydrogen partial pressure is preferably about 100 to about 1100 kPa (about 15 to about 160 psia) and more preferably from about 210 to about 690 kPa (about 30 to about 100 psia). In general the H_2:CO molar ratio of gaseous hydrogen to carbon monoxide may range from about 1:10 to 100:1 or higher, the more preferred hydrogen to carbon monoxide molar ratio being from about 1:1 to about 10:1.

Further as noted above the hydroformylation process of this invention may be conducted at a reaction temperature from about 45°C to about 200°C. The preferred reaction temperature employed in a given process will of course be dependent upon the particular olefinic starting material and metal catalyst employed as well as the efficiency desired. While conventional hydroformylation reaction temperatures may also be employed herein, the operation of the hydroformylation process of this invention can be optimized in a surprisingly lower temperature range than heretofore preferably advanced by the prior art.

For example, compared to prior art rhodium catalyzed hydroformylation systems, the improved catalytic activity and/ or stability afforded by the rhodium-diorganophosphite complex catalysts of this invention is particularly unique for achieving high rates of selective hydroformylation at comparatively low reaction temperatures. In general, hydroformylations at reaction temperatures of about 50°C to about 120°C are preferred for all types of olefinic starting materials. More preferably, α-olefins can be effectively hydroformylated at a temperature of from about 60°C to about 110°C while even less reactive olefins than conventional α-olefins such as isobutylene and internal olefins as well as mixtures of α-olefins and internal olefins are effectively and preferably hydroformylated at a temperature of from about 70°C to about 120°C. Indeed in the rhodium-catalyzed hydroformylation process of this invention no substantial benefit is seen in operating at reaction temperatures much above 120°C and such is considered to be less desirable, due to possible catalyst activity decline and/or rhodium losses that may be caused by the higher temperatures.

As outlined herein the hydroformylation process of this invention can be carried out in either the liquid or gaseous state and involve a continuous liquid or gas recycle system or combination of such systems. Preferably the rhodium catalyzed hydroformylation of this invention involves a continuous homogeneous catalysis process wherein the hydroformylation is carried out in the presence of both free diorganophosphite ligand and any suitable conventional solvent as further outlined herein. Such types of continuous hydroformylation systems and methods for carrying them out are well known in the art and thus need not be particularly detailed herein.

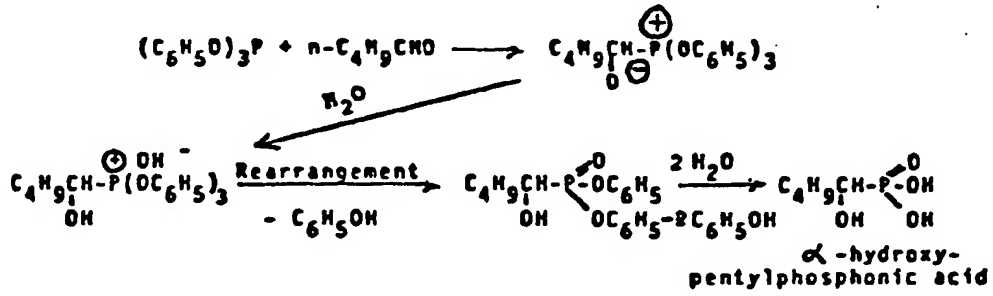
While the hydroformylation process of this invention may be carried out employing any olefinic unsaturated starting material such as already noted herein, the preferred rhodium catalyzed hydroformylation process of this invention has been found to be particularly effective in converting olefins such as α-olefins having from 2 to 20 carbon atoms and internal olefins having from 4 to 20 carbon atoms, as well as mixtures of such olefins, to their corresponding aldehyde products. Moreover, the hydroformylation of olefins that are normally less reactive than their corresponding sterically unhindered α-olefins, such as isobutylene and internal olefins is an even more preferred aspect of this invention, as is the hydroformylation of mixtures of α-olefins and internal olefins.

In general the use of the diorganophosphite ligands provide a far more catalytically active and stable rhodium catalyst for the hydroformylation of olefins, especially internal and other such less reactive sterically hindered olefins e.g. isobutylene than obtainable with conventional triorganophosphine ligands, thus allowing for greater rates and/or increased amounts of aldehyde production at much lower reaction temperatures. The rhodium catalyzed hydroformylation process of this invention of mixtures of α-olefins and internal olefins is further unique in that the subject process of this invention results in a high degree of aldehyde product production from both types of olefins in the starting material, in contrast to those prior art processes that promote hydroformylation of primarily only the more reactive sterically unhindered α-olefins. Of course, it is to be understood that the proportional make up of the mixed olefin starting materials employable in this invention is not critical and any desired proportional amounts of such olefins may be employed in the starting olefin mixture. In general, it is especially preferred to hydroformylate mixtures of butene-1 and butene-2 (cis and/or trans), which mixtures may also optionally contain isobutene, in order to obtain proportionate product mixtures of valeraldehyde, 2-methylbutyraldehyde and optionally 3-methylbutyraldehyde.

Further, undesirable side reactions that may occur in rhodium catalyzed hydroformylation may be curtailed by the use of the diorganophosphite ligands of this invention such as, undue aldehyde by-product heavies formation, as well as ligand stability towards the aldehyde product. For example, while the use of the diorganophosphite ligands employable herein may curtail undue higher boiling aldehyde condensation by-product formation, it is axiomatic that in commercial continuous hydroformylation of such olefins the concentration of such higher boiling aldehyde condensation by-products (e.g. dimeric and trimeric aldehydes) will eventually continue to build over a period of time until it is finally desirable or necessary to remove at least a portion of such higher boiling aldehyde condensation by-products, as described e.g. in US-A-4,148,430 and 4,247,486. In such an occurrance it is desirable that phosphorus ligand which is also present (preferably in an excess amount) have a lower vapor pressure (higher boiling point) than that of the aldehyde condensation by-products so that the ligand will not be lost or depleted when such aldehyde condensation by-products are removed. For example, volatility is related to molecular weight and is

inversely proportional to molecular weight within a homologous series. Accordingly, it is desirable to employ a diorganophosphite ligand whose molecular weight exceeds that of the aldehyde by-product trimer corresponding to the aldehyde being produced. For instance, since the molecular weight of valeraldehyde trimer is about 258 ($C_{15}H_{30}O_3$) and all the preferred diorganophosphites of this invention exceed 330 in molecular weight, it is clear that the diorganophosphites of this invention are especially suitable for use in hydroformylating butene-1 and/or butene-2, is as much as there should not be any considerable loss of the diorganophosphite ligand during product aldehyde and higher boiling aldehyde by-product removal, as might predictably be the case when a different phosphorus ligand having a lower molecular weight (e.g. higher vapor pressure or lower boiling point) than the higher boiling aldehyde by-product is employed (and which would require additional processing steps if recovery and reuse of the phosphorus ligand is desired).

Further, while triorganophosphite ligands in general will provide a metal-complex catalyst with sufficient activity to hydroformylate internal olefins, experience has shown that their use, particularly with regard to continuous hydroformylation, has been less than satisfactory. This drawback in employing triorganophosphites is believed to be due to their very high affinity for reacting with aldehydes, the product of which has been found to readily hydrolyze to a corresponding hydroxy alkyl phosphonic acid, as shown by the following skeletal reaction mode:



Moreover, the formation of such acid is an autocatalytic process, thus rendering triorganophosphite ligands even more susceptible to the production of such undesirable acid by-products, particularly in continuous rhodium catalyzed liquid recycle hydroformylation wherein contact between the phosphite ligand and aldehyde product is prolonged. Surprisingly, the diorganophosphite ligands employable in this invention have been found in general to be far less moisture sensitive and far less reactive toward forming such phosphonic acid than conventional triorganophosphites, thus providing a more prolonged stable and active continuous rhodium catalyzed liquid recycle hydroformylation than may be possible with triorganophosphite ligands. Such is not to say however, that hydroxy alkyl phosphonic acid by-product will not be eventually formed over the course of the continuous rhodium catalyst liquid recycle hydroformylation process of this invention. However, the accumulation of such undesirable hydroxy alkyl phosphonic acid, during a continuous recycle hydroformylation process of this invention, takes place at a much slower rate than when triorganophosphite ligands are employed, which allows for a longer and more efficient continuous operation. For instance, rapid decomposition of the phosphite ligand may not only adversely affect catalyst activity and/or stability, but obviously leads to a quick loss of the phosphite ligand that must be replaced with make-up phosphite ligand, as well as helps to further promote the autocatalytic formation of the undesirable hydroxy alkyl phosphonic acid which is often insoluble in the general liquid hydroformylation reaction medium. Consequently rapid and high build-up of such hydroxy alkyl phosphonic acid can lead to precipitation of the acid to an obviously undesirable gellatinous by-product, which may plug and/or foul the recycle lines of a continuous liquid reaction system, thus necessitating periodic processing shut-downs or stoppages for removal of such acid and or precipitate from the system by any appropriate method e.g. by extraction of the acid with a weak base, e.g. sodium bicarbonate.

Moreover, it has been surprisingly found that the above mentioned disadvantages attendent with such hydroxy alkyl phosphonic acid by-product may be effectively and preferably controlled by passing the liquid reaction effluent stream of a continuous liquid recycle process either prior to or more preferably after separation of the aldehyde product therefrom through any suitable weakly basic anion exchange resin, such as a bed of amine-Amberlyst® resin, e.g. Amberlyst® A-21, and the like, to remove some or all of the undesirable hydroxy alkyl phosphonic acid by-product that might be present in the liquid catalyst containing stream prior to its reincorporation into the hydroformylation reactor. Of course if desired, more than one such basic anion exchange resin bed, e.g. a series of such beds, may be employed and any such bed may

be easily removed and/or replaced as required or desired. Alternatively if desired, any part or all of the hydroxy alkyl phosphonic acid contaminated catalyst recycle stream may be periodically removed from the continuous recycle operation and the contaminated liquid so removed treated in the same fashion as outlined above, to eliminate or reduce the amount of hydroxy alkyl phosphonic acid contained therein prior to reusing the catalyst containing liquid in the hydroformylation process. Likewise, any other suitable method for removing such hydroxy alkyl phosphonic acid by-product from the hydroformylation process of this invention may be employed herein if desired.

Accordingly another preferred and novel aspect of the subject invention is directed to an improved continuous hydroformylation process for producing aldehydes which comprises reacting an olefin with carbon monoxide and hydrogen in the presence of a liquid-medium containing a solubilized rhodium-organophosphite complex catalyst, a solvent, free organophosphite ligand, and aldehyde product, the improvement comprising minimizing decomposition of the free organophosphite ligand by (a) removing a stream of said liquid medium from the hydroformylation reaction zone, (b) treating the liquid medium so removed with a weakly basic anion exchange resin and (c) returning the treated reaction medium to the hydroformylation reaction zone.

Such treatment of the liquid medium with a weakly basic anion exchange resin comprises passing the liquid medium, i.e., liquid reaction effluent stream, after removal of said stream from the hydroformylation reaction zone, either prior to and/or after separation of aldehyde product therefrom, through a weakly basic anion exchange resin bed.

Any suitable weakly basic anion exchange resin bed may be employed herein. Illustrative weakly basic anion exchange resin beds employable herein may include, e.g., crosslinked tertiary amine polystyrene anion exchange resins of the gel or macroreticular type, such as a bed of amine-Amberlyst® resin and more preferably, Amberlyst® A-21, which comprises a crosslinked polystyrene backbone with pendant benzyl dimethylamino [$-C_6H_4-CH_2-N(CH_3)_2$] functional groups. Such types of weakly basic anion exchange resin beds and/or methods for their manufacture are well known in the art.

As noted above decomposition of the organophosphite ligand may be effectively controlled and minimized by the preferred treatment of this invention which as postulated removes some or all of the undesirable hydroxy alkyl phosphonic acid by-product that might be present in the liquid medium as a result of in situ build-up over the course of the hydroformylation reaction and which is an autocatalytic material for decomposition of the organophosphite, e.g., via the side reaction of phosphite ligand and aldehyde product.

While small amounts of such hydroxyalkyl phosphonic acids in hydroformylation reaction mediums are difficult to analyze for by standard analytical methods such as gas chromatography or liquid chromatography due in part to the high boiling points and polar nature of such acids; ^{31}P NMR (Nuclear Magnetic Resonance) can be successfully employed to detect such acids in amounts as low as about 100 ppm by weight. For example, one need only determine the detectable resonance peak (chemical shift in ppm relative to external H_3PO_4) via ^{31}P NMR for a comparative synthetic solution containing 100 ppm of the hydroxyalkyl phosphonic acid, then monitor the hydroformylation reaction medium of the process in question for evidence of the corresponding acid resonance peak via the same ^{31}P NMR technique. Thus while the subject improvement generically encompasses a process for removal of hydroxyalkyl phosphonic acid from a liquid hydroformylation reaction medium that already contains more than merely a trace amount of such acid to thereby minimize further decomposition of the organophosphite ligand, experience has shown that decomposition of the organophosphite ligand can be very rapid when the amount of hydroxy alkyl phosphonic acid is allowed to build up to more than a trace amount. Thus the preferred process of this invention is one in which the liquid medium to be treated does not even contain a readily detectable amount of such hydroxy alkyl phosphonic acid and such is accomplished by beginning said treatment of the liquid medium prior to the build-up of a readily detectable amount (e.g. 100 ppm) by weight of such hydroxy alkyl phosphonic acid via ^{31}P NMR so as to remove said hydroxy alkyl phosphonic acid as it is being formed. Accordingly, while this invention encompasses both intermittent and continuous treatment of the liquid medium to minimize organophosphite ligand decomposition, continuous treatment of the liquid medium during the hydroformylation process is preferred.

Moreover the minimization of the degree of decomposition of the organophosphite ligand obtainable by the process of this invention can be readily observed and quantitatively calculated if desired, by determining in a given process, the amount of organophosphite ligand remaining and/or lost in the hydroformylation reaction medium, from that amount initially employed, after a given period of time of the continuous hydroformylation process, in contrast to the amount of organophosphite ligand remaining and/or lost in a corresponding continuous hydroformylation process carried out under the same conditions, but without employing the weakly basic anion exchange resin treatment outlined herein.

Accordingly minimizing the degree of decomposition of the organophosphite ligand by preventing and/or slowing down the rate of reaction between such ligands and aldehyde product, allows for a longer and more efficient continuous operation than a comparative hydroformylation process carried out in the absence of a weakly basic onion exchange resin treatment. Moreover in addition to preventing and/or minimizing ligand and aldehyde product loss, the subject treatment may also help sustain the rate of hydroformylation and aldehyde product ratio desired over a longer period of time, as well as help maintain catalyst activity and/or stability, which may be adversely affected by rapid decomposition of the organophosphite ligand. Further the drawback of rapid and high build-up of such hydroxy alkyl phosphonic acid which can lead to precipitation of the acid to an obviously undesirable gellatinous by-product and which may plug and/or foul the recycle lines of a continuous hydroformylation system can be overcome by the process of this invention.

The employment of a weakly basic anion exchange resin as described in this invention is indeed unique and surprising, since such resins, e.g., Amberlyst® A-21 are known to be highly reactive with carboxylic acids, which are also minor oxo reaction by-products. This property alone would suggest that the use of such resins would not be a practical means for the removal of phosphonic acid from a hydroformylation process stream, since it suggests that the acid neutralization ability of the resin would be consumed too rapidly by the carboxylic acid generated by the hydroformylation. However, it has been surprisingly found that the carboxylic acid neutralized form of Amberlyst® A-21 resin is still basic enough, to remove the stronger hydroxyalkyl phosphonic acid from hydroformylation streams even in the presence of carboxylic acids. Moreover, experience has shown that the addition of tertiary amines (such as dimethylaniline, triethanolamine, proton sponge, etc.) to phosphite ligand promoted rhodium complex hydroformylation catalysts can cause rapid rhodium precipitation in the form of black solids. Likewise, Amberlyst® A-21 resin itself when added to a hydroformylation reaction medium under hydroformylation conditions has been found to cause rhodium precipitation on the resin surface and pores. It is therefore clearly unexpected and fortunate that the use of a weakly basic anion exchange resin as described herein, e.g., Amberlyst® A-21 on a liquid medium stream that has been removed from the hydroformylation reaction zone does not adversely precipitate rhodium or unduly adversely affect the rhodium catalyst and process in any significant adverse manner, such as by increasing the rate of aldehyde heavies formation.

It is to be noted, however, that commercial grade weakly basic anion exchange resin beds, such as Amberlyst® A-21, may contain halide impurities, e.g. chloride contaminates, which are known to poison (adversely affect) rhodium complex hydroformylation catalysts. Thus it is preferred that the weakly basic anion exchange resin beds employable herein be at least substantially free of halogen contaminates and more preferably essentially or entirely free from such halogen contaminates. Removal of such halogen contaminates, as well as any other undesirable contaminates, from such weakly basic anion exchange resin beds prior to their use may be readily accomplished by conventional washing techniques that are well known in the art.

As further noted herein the treatment of the liquid medium containing a solubilized rhodium-organophosphite complex catalyst, a solvent, free organophosphite ligand and aldehyde product must take place outside of the hydroformylation reaction zone of the continuous hydroformylation process and the medium so treated returned to the hydroformylation reactor. Accordingly, this treatment is adaptable to both well known continuous type gas and/or liquid recycle hydroformylation processes.

For example, in a continuous gas recycle hydroformylation process, the treatment of this invention may be carried out by intermittently or continuously withdrawing a portion e.g. slip stream of the liquid reaction mixture from the reactor, passing it through a weakly basic anion exchange resin bed and returning the so treated slip stream of the liquid reaction mixture to the reactor. In a liquid recycle hydroformylation process, the liquid medium removed from the reactor can be passed through the weakly basic anion exchange resin bed at any point throughout the recycle process. For instance, in a liquid recycle hydroformylation procedure, it is common place to continuously remove a portion of the liquid reaction product medium from the reactor and the desired aldehyde product recovered in one or more distillation stages e.g. by passing said liquid medium to a vaporizor/separator wherein the desired product is distilled and separated from said medium and eventually condensed and recovered. The remaining liquid residue obtained upon such separation of aldehyde product, which residue contains the rhodium-organophosphite catalyst, solvent, free organophosphite ligand and some undistilled aldehyde product is then recycled back to the reactor along with whatever by-products e.g. hydroxy alkyl phosphonic acid that might also be present in said recycled residue. While the treatment of such liquid mediums, of such continuous liquid recycle hydroformylation processes, according to this invention can be carried out prior to and/or subsequent to the separation of aldehyde product therefrom, it is preferred to carry out the treatment of this invention after the removal or separation of aldehyde product. For example, it is preferred to position the weakly basic anion exchange

resin bed after the aldehyde product vaporizor/separator so that what is passed through the weakly basic anion exchange resin bed is the catalyst containing liquid recycle residue as explained above. In addition to being a more convenient and economical position in the reaction system for utilizing such a weakly basic anion exchange resin bed, it is believed that such positioning minimizes the amount of the hydridic form of the rhodium catalyst which is to come in contact with the weakly basic anion exchange resin,and it is the hydridic form of the rhodium catalyst that is believed to be the reactive form which in the presence of e.g. amines may form insoluble anionic rhodium clusters. It is believed that the hydridic form of the rhodium catalyst is changed to a less reactive non-hydridic form as it passes through the aldehyde product recovery distillation stage, e.g. vaporizor/separator, of the hydroformylation process and that this less reactive rhodium catalyst form is less likely to cause process complications when contacted with the weakly basic anion exchange resin.

In view of the fact that the weakly basic anion exchange resin treatment encompassed herein is designed to obtain a desired improvement in at least minimizing the degree of decomposition of the organophosphite ligand employed in the hydroformylation process over that experienced in the absence of such a resin treatment, it is apparent that specific values cannot be arbitrarily given to such conditions as the design, number and positioning of the resin bed in the reaction system, temperature and contact time for the treatment. Such conditions are not narrowly critical and obviously need only be at least sufficient to obtain the improvement desired. For instance, the subject invention contemplates the employment of any conventional anion exchange resin bed design through which the liquid medium to be treated may be passed, and any such bed may be easily removed and/or replaced as desired. Moreover, the number of beds employed, as well as their positioning in the reaction system involved is also not considered absolutely critical and need only be such that is suitable to obtain the result desired. Likewise, treatment conditions such as temperature, pressure and contact time may also vary greatly depending on the wishes of the operator and any suitable combination of such conditions may be employed herein so long as the desired effectiveness of the treatment is achieved. Likewise, the treatment is preferably carried out under normal operating pressures within the system employed although higher or lower pressures may be employed if desired, while the contact time of the liquid medium passing through the resin bed is normally only a matter of seconds.

Of course, it is to be understood that while the selection of the optimum levels and conditions of such variables as discussed above are dependent upon one's experience in the utilization of the subject resin treatment, only a certain measure of experimentation should be necessary in order to ascertain those conditions which are optimum for a given situation. For example, since the preferred subject invention is directed to a continuous hydroformylation process in which decomposition of the organophosphite ligand employed will be prevented and/or minimized for as long as possible, and since such decomposition is considered to be accelerated by the build-up of undesirable hydroxy alkyl phosphonic acid by-product, it is obviously preferred and beneficial to have the weakly basic anion exchange resin bed in place, at the start-up of the hydroformylation process involved, or in place soonly thereafter, so that the liquid medium to be treated can be continuously passed through the resin bed, thus preventing any undue build-up of undesirable acid by-product as discussed above. Of course, if desired, the resin bed can be used later on in the process to remove readily detectable amounts of such hydroxy alkyl phosphonic acid by-product build-up, although such is a less desirable way of minimizing decomposition of the organophosphite ligand.

Moreover, the diorganophosphite ligands employable herein have the added benefit of improved storage stability or shelf-life over that of conventional triorganophosphites, such as trialkylphosphites, e.g. trimethylphosphite, triethylphosphite, and the like, and triarylphosphites e.g. triphenylphosphite, tris (2-biphenyl) phosphite and the like, particularly with regard to moisture sensitivity and hydrolytic stability.

Thus it should be clear that one of the featured beneficial factors involved in the employment of the diorgano phosphite ligands in this invention, in contrast to that heretofore employed in the prior art, is the wide processing latitude as taught herein that one has in selecting the proper combination of conditions that will be most useful in obtaining or at least best approaching a particular desired result or need.

Thus while it is clear that the rhodium hydroformylation process of this invention represents a clear technical advancement in the art, it should be noted that some rhodium loss, i.e. precipitation of the rhodium from solution, has been found to occur in the continuous liquid recycle hydroformylation process of this invention. It is believed that such rhodium loss has been caused by high temperatures employed in separating the desired aldehyde product from the rhodium catalyst containing product solution and that such rhodium loss may be reduced, if not eliminated, by separating the desired aldehyde product from the rhodium catalyst containing product solution under reduced pressure and at low temperatures such as below 130 °C. and more preferably below 110 °C.

In addition to providing the basic benefits of catalyst reactivity and stability in the hydroformylation of

olefins to aldehydes as outlined hereinabove, the diorganophosphite ligands of Formulas (V) and (VI) above, as well as the rhodium complex catalysts containing such diorganophosphite ligands of Formulas (V) and (VI) above, are considered to be novel compositions of matter and uniquely beneficial in that they may allow for the use of higher aldehyde vaporization (separation) temperatures in the continuous liquid recycle hydroformylation process of this invention then heretofore considered preferred. For instance, as noted above, some rhodium loss has previously been experienced in some continuous liquid recycle hydroformylation process experiments and such loss has been attributed in part to the vaporization temperature employed in separating the desired aldehyde product from the rhodium catalyst containing product solution. Accordingly, heretofore it has been recommended that such separation of the desired aldehyde product be preferably conducted at below 110°C to avoid such rhodium loss. It has now been surprisingly found that such separation of the desired aldehyde product may preferably be conducted at even higher temperatures, e.g. up to 120°C, and possibly even higher, when a diorganophosphite ligand of Formulas (V) or (VI) is employed as witnessed by an experiment wherein no rhodium loss was observed over a prolonged period of continuous hydroformylation and at such a higher preferred aldehyde vaporization (separation) temperature, when methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1-biphenyl-2,2'diyl] phosphite was employed. Of course, the benefits attributable to a continuous process wherein the loss of rhodium is prevented or at least minimized over a long period of time and those attributable to being able to employing a higher temperature for separating the desired aldehyde product from the catalyst containing reaction solution without the attendent drawback of rhodium loss are self-evident. The higher the aldehyde separation temperature employed the more aldehyde product one may recover per given unit of time. In turn, the ability to be able to separate more aldehyde product more quickly, allows for greater processing control with regard to the build-up of higher boiling aldehyde condensation by-products that take place during the hydroformylation process, thus providing an effective means for eliminating and/or minimizing any adverse build-up of such higher boiling aldehyde condensation by-products.

In addition, the diorganophosphite ligands of Formulas (V) and (VI) above and the rhodium complex catalysts containing such ligands are believed to be more soluble in the hydroformylation reaction medium than the diorganophosphite compound counterparts of the same type wherein the Z^2 and Z^3 groups of the above formulas are hydrocarbon radicals (e.g. t-butyl) instead of the ether (i.e. oxy) groups, such as hydroxy and/or $-OR^6$ as defined in said Formulas (V) and (VI) above. While not wishing to be held to any theory or mechanistic discourse, such ligand solubility may be the reason no rhodium loss was observed over a prolonged period of time at an aldehyde separation temperature higher than heretofore recommended as preferred when methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite was employed. Alternatively, rhodium complex catalysts containing a ligand as defined in said Formulas (V) and (VI) above may undergo some structural change under hydroformylation and/or vaporizer/separation conditions to a more stable or soluble rhodium complex due to the ether (i.e. oxy) groups represented by Z^2 and Z^3 in Formulas (V) and (VI) above.

Moreover, while the diorganophosphite ligands of Formulas (V) and (VI) above and the rhodium complex catalysts containing such a diorganophosphite ligand are considered to be novel compositions of matter, it is of course to be understood that such ligands and catalysts can be readily made by the same general procedures, disclosed elsewhere herein, for obtaining diorganophosphite ligands and rhodium complex catalysts in general. Likewise diorganophosphites wherein Z^2 and Z^3 of Formulas (V) and (VI) are hydroxy groups can be readily prepared by first obtaining the corresponding ligand wherein Z^2 and Z^3 are an alkoxy (e.g. benzyloxy) group followed by any conventional dealkylation procedure (e.g. hydrogenolysis).

A further aspect of this invention can be described as a catalyst precursor composition consisting essentially of a solubilized rhodium-diorganophosphite complex precursor catalyst, an organic solvent and free diorganophosphite ligand. Such precursor compositions may be prepared by forming a solution of a rhodium starting material, such as a metal oxide, hydride, carbonyl or salt e.g. a nitrate, which may or may not be in complex combination with a diorganophosphite ligand, an organic solvent and a free diorganophosphite ligand as defined herein. Any suitable rhodium starting material may be employed e.g. rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$, diorganophosphite rhodium carbonyl hydrides, as well as carboxylates of C_2-C_{16} acids. Of course any suitable solvent may be employed such as e.g. those employable in the hydroformylation process desired to be carried out. The desired hydroformylation process may of course also dictate the various amounts of metal, solvent and ligand present in the precursor solution. Carbonyl and diorganophosphite ligands if not already complexed with the initial rhodium may be complexed to the metal either prior to or in situ during the hydroformylation process. The preferred catalyst precursor composition of this invention consists essentially of a solubilized rhodium carbonyl diorganophosphite acetylacetonate complex precursor catalyst, an organic solvent and free diorganophosphite ligand. Such precursor compositions are prepared by forming a solution of rhodium

dicarbonyl acetylacetonate, an organic solvent and a diorganophosphite ligand as defined herein. The diorganophosphite readily replaces one of the dicarbonyl ligands of the rhodium-acetylacetonate complex precursor at room temperature as witnessed by the evolution of carbon monoxide gas. This substitution reaction may be facilitated by heating the solution if desired. Any suitable organic solvent in which both the rhodium dicarbonyl acetylacetonate complex precursor and rhodium carbonyl diorganophosphite acetylacetonate complex precursor are soluble can be employed. Accordingly, the amounts of rhodium complex catalyst precursor, organic solvent and diorganophosphite, as well as their preferred embodiments present in such catalyst precursor compositions may obviously correspond to those amounts employable in the hydroformylation process of this invention and which have already been discussed herein. Experience has shown that the acetylacetonate ligand of the precursor catalyst is replaced after the hydroformylation process has begun with a different ligand, e.g. hydrogen, carbon monoxide or diorganophosphite ligand, to form the active rhodium complex catalyst as explained above. The acetylacetone which is freed from the precursor catalyst under hydroformylation conditions is removed from the reaction medium with the product aldehyde and thus is in no way detrimental to the hydroformylation process. The use of such preferred rhodium complex catalytic precursor compositions thus provides a simple economical and efficient method for handling the rhodium precursor metal and hydroformylation start-up.

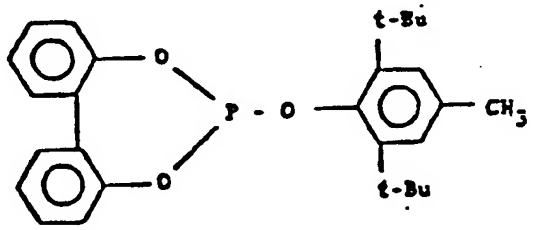
Finally, the aldehyde products of the hydroformylation process of this invention have a wide range of utility that is well known and documented in the prior art e.g. they are especially useful as starting materials for the production of alcohols and acids.

The following examples are illustrative of the present invention and are not to be regarded as limitative. It is to be understood that all of the parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

A series of various rhodium complex catalyst precursor solutions consisting essentially of solubilized rhodium carbonyl diorganophosphite acetylacetonate complex precursor catalyst, organic solvent and free diorganophosphite ligand were prepared and employed to hydroformylate trans butene-2 into C_6 aldehydes in the following manner.

Rhodium dicarbonyl acetylacetonate was mixed with sufficient 1,1'-biphenyl-2,2'-diyl-(2,6-di-tertiarybutyl-4-methylphenyl)phosphite ligand having the formula



the amount of ligand being varied in each instance as shown in TABLE 1 below) and diluted with sufficient solvent Texanol® (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) to produce the various rhodium catalytic precursor solutions containing the amounts of rhodium and ligand shown in TABLE 1 below.

Each rhodium catalytic precursor solution so prepared was then employed to hydroformylate trans-butene-2 in a magnetically stirred, 100 ml capacity, stainless steel autoclave which was attached to a gas manifold for introducing gases to the desired partial pressures. The autoclave was also equipped with a pressure calibrator for determining reaction pressure to ± 0.07 kPa (± 0.01 psia.) and a platinum resistance thermometer for determining reactor solution temperatures to ± 0.1 °C. The reactor was heated externally by two 300 watt heating bands. The reactor solution temperature was controlled by a platinum resistance sensor connected to an external proportional temperature controller for controlling the temperature of the external band heaters.

In each hydroformylation reaction, about 20 milliliters of the rhodium catalytic precursor solution so prepared containing the rhodium complex, the diorganophosphite ligand and the solvent was charged to the autoclave reactor under nitrogen and heated to the reaction temperature employed (as given in TABLE 1 below). The reactor was then vented down to 0.134 MPa (5 psig.)and 5 ml (2.9 grams) of trans-butene-2 introduced into the reactor. Then carbon monoxide and hydrogen (partial pressures given in Table 1) were

introduced into the reactor via the gas manifold and the trans-butene-2 so hydroformylated.

The hydroformylation reaction rate in gram moles per liter per hour of C_5 aldehydes produced was determined from sequential 34.5 kPa (5 psia.) pressure drops in the reactor spanning the nominal operating pressure in the reactor, while mole ratio of linear (n-valeraldehyde) to branched (2-methylbutyraldehyde) product was measured by gas chromatography and the results are given in TABLE 1 below, said results being determined after about a 5 to 20 percent conversion of the trans-butene-2 starting material.

TABLE 1

Run No.	Temp. °C	Rh, ppm	Ligand/ Rhodium Mole Ratio	Partial Pressure H_2 H_2 (psia)	Partial Pressure CO H_2 (psia)	trans-butene-2 moles	Reaction Rate Gram Moles/ Liter/Hour	Linear/Branched C5 Aldehyde Mole Ratio
1	100	25	10	0.24 (30)	0.21 (30)	50	2.94	0.68
2	100	50	10	0.21 (30)	0.21 (30)	50	5.73	0.71
3	100	250	10	0.21 (30)	0.21 (30)	50	4.63	0.77
4	100	500	10	0.21 (30)	0.21 (30)	50	4.95	0.86
5	100	250	3	0.21 (30)	0.21 (30)	50	17.19	0.75
6	100	250	9	0.24 (30)	0.21 (30)	50	5.73	0.79
7	100	250	18	0.21 (30)	0.21 (30)	50	2.96	0.76
8	100	250	10	0.21 (30)	0.10 (15)	50	3.78	1.0
9	100	250	10	0.21 (30)	0.41 (60)	50	6.68	0.76
10	100	250	10	0.21 (30)	0.62 (90)	50	7.76	0.83
11	100	250	10	0.10 (15)	0.21 (30)	50	3.55	1.01
12	100	250	10	0.41 (60)	0.21 (30)	50	7.29	0.82
13	100	250	10	0.62 (90)	0.21 (30)	50	7.93	0.78
14	70	250	10	0.21 (30)	0.21 (30)	50	0.64	0.24
15	130	250	10	0.14 (30)	0.21 (30)	50	12.85	1.13

EXAMPLE 2

The same procedure and conditions employed in Example 1 of preparing a rhodium catalytic precursor solution using rhodium dicarbonyl acetylacetonate. Texanol® and 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite ligand and hydroformylating trans-butene-2 were repeated save for the exceptions of hydroformylating butene-1 instead of trans-butene-2 and using about 15 milliliters of the rhodium precursor solution instead of 20 milliliters and varying the rhodium complex catalyst precursor solutions and hydroformylation reaction conditions as shown in TABLE 2 below. The hydroformylation reaction rate in terms of gram moles per liter per hour of C_5 aldehydes produced as well as the mole ratio of linear (n-valeraldehyde) to branched (2-methylbutyraldehyde) product were determined in the same manner as in Example 1 and the results are given in TABLE 2 below.

TABLE 2

Run No.	Temp. °C	Rh, ppm	Ligand/ Rhodium Mole Ratio	Partial Pressure H_2 (psia)	Partial Pressure CO (psia)	butene-1 m moles	Reaction Rate Gram Moles/ Liter/Hour	Linear/Branched C_5 Aldehyde Mole Ratio
1	100	200	10	0.14 (20)	0.14 (20)	50	0.78	2.16
2	100	200	10	0.41 (60)	0.41 (60)	50	14.5	2.30
3	50	250	5	0.41 (60)	0.41 (60)	50	2.42	2.51
4	70	50	10	0.21 (30)	0.21 (30)	50	2.37	2.48
5	100	25	5	0.21 (30)	0.21 (30)	50	1.23	1.51
6	120	50	20	0.21 (30)	0.21 (30)	50	3.41	1.14

EXAMPLE 3

The same procecure and conditions employed in Example 1 of preparing a rhodium catalytic precursor solution using rhodium dicarbonyl acetylacetonate. Texanol® and 1,1'-biphenyl-2,2'- diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite ligand and hydroformylating trans-butene-2 were repeated, save for the exceptions of using the various organophosphite ligands and varying the rhodium complex catalyst precursor solutions and hydroformylation reaction conditions as shown in TABLE 3 below. The hydroformylation reaction rate in terms of gram moles per liter per hour of C_5 aldehydes (pentanals) produced as well as the mole ratio of linear (n-valeraldehyde) to branched (2-methylbutyraldehyde) product were determined in the same manner as in Example 1 and the results are given in TABLE 3 below.

TABLE 3

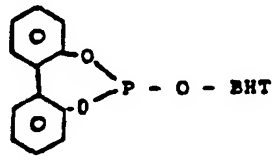
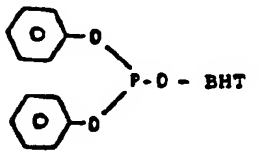
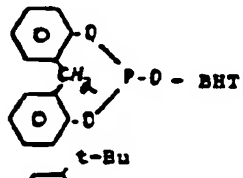
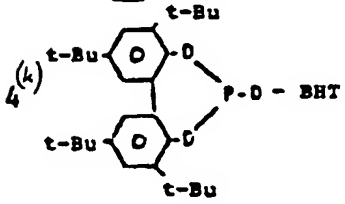
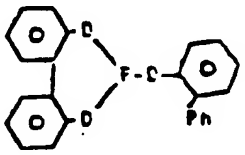
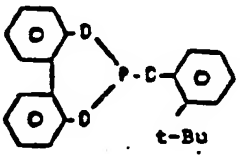
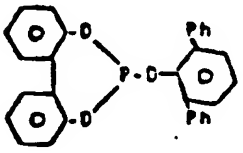
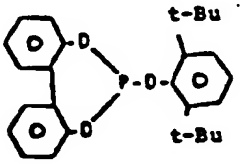
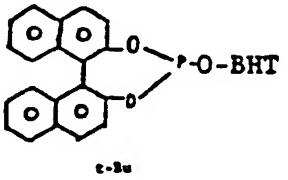
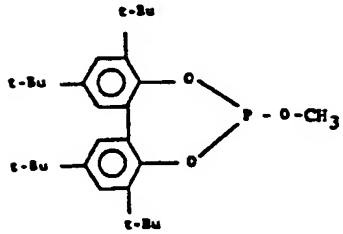
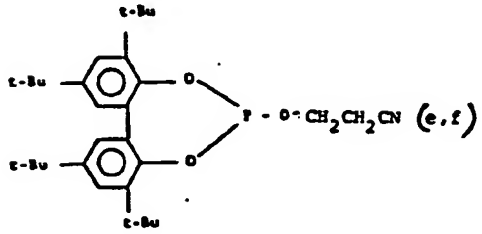
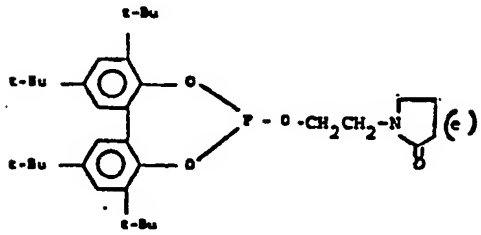
Run No.	Ligand (g)	Precursor Solution and Reaction Conditions	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
1		(b)	4.7	0.7
2		(b)	3.4 (h)	0.89
3		(b)	17.82(i)	0.86
4(k)		(b)	0.46	0.56

TABLE 3 (CONTINUED)

Run No.	Ligand (g)	Precursor Solution and Reaction Conditions	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
5		(c)	1.1 (j)	1.0
6		(c)	2.9 (j)	1.0
7		(c)	2.6 (j)	1.0
8		(c)	8.1	0.73

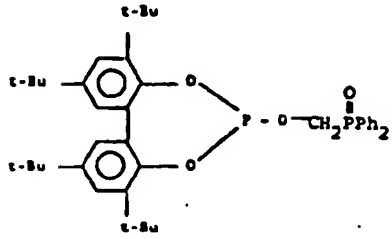
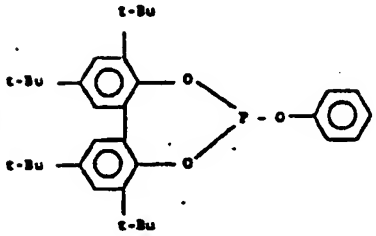
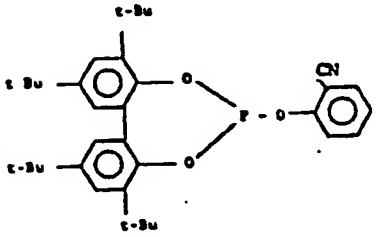
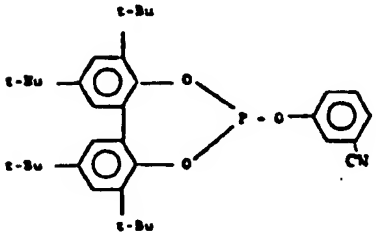
(Continued next page)

TABLE 3 (CONTINUED)

Run No.	Ligand (g)	Precursor Solution and Reaction Conditions	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
9		(a)	4.5	1.12
10		(e,f)	5.4	0.68
11		(e,f)	0.65	0.68
12		(e)	0.51	0.62

(Continued next page)

TABLE-3 (CONTINUED)

Run No.	Ligand (g)	Precursor Solution and Reaction Conditions	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
13		(e,f)	0.92	0.67
14		(d)	8.7	0.82
15		(d)	4.0	0.88
16		(d)	7.6	1.1

(Continued next page)

(a) Precursor solution and reaction conditions: 200 ppm rhodium: 6 moles diorganophosphite ligand per mole of rhodium; reaction temperature 100°C.; partial pressures; H_2 = 20 psia., CO = 20 psia, trans-butene-2 = 50 m moles. (20 psia = 0.14 MPa)

(b) Precursor solution and reaction conditions: 200 ppm rhodium; 10 moles diorganophosphite ligand per mole of rhodium; reaction temperature 105°C.; partial pressures, H_2 = 30 psia, CO = 30 psia, trans-butene-2 = 50 m moles. (30 psia = 0.21 MPa)

(c) Precursor solution and reaction conditions: 230 ppm rhodium; 3 moles diorganophosphite ligand per mole of rhodium; reaction temperature 100°C.; partial pressures, H_2 = 20 psia, CO = 20 psia, trans-butene-2 = 50 m moles. Used 15 milliliter rhodium catalytic precursor solution instead of 20 milliliters. (20 psia = 0.14 MPa)

(d) Precursor Solution and reaction conditions: 200 ppm rhodium; 10 moles diorgano-phosphite ligand per mole of rhodium; reaction temperature 105°C.; partial pressures, H_2 = 30 psia., CO = 30 psia, trans-butene-2 = 50 m moles. Used 15 milliliters rhodium catalytic precursor solution instead of 20 milliliters. (30 psia = 0.21 MPa)

(e) Precursor solution and reaction conditions: 200 ppm rhodium; 6 moles diorganophosphite ligand per mole of rhodium; reaction temperature 100°C; partial pressures, H_2 = 20 psia, CO = 20 psia, trans-butene-2 = 50 m moles. Used 15 milliliters rhodium catalytic precursor solution instead of 20 milliliters. (20 psia = 0.14 MPa)

(f) Used $Rh_4(CO)_{12}$ as rhodium precursor instead of rhodium dicarbonyl acetylacetonate.

(g) BHT = 2,6-di-tert-butyl-4-methylphenyl
t-Bu = tertiary-butyl
Ph = phenyl

(Continued next page)

TABLE 3 (CONTINUED)

(h) Activity of this comparative triorganophosphite promoted catalyst rapidly declined under continuous hydroformylation (See Example 5).

(i) Activity of this diorganophosphite promoted catalyst declined very rapidly in a continuous glass reactor experiment similar to that described in Example 5.

(j) The activity of these diorganophosphite promoted catalysts was sharply inhibited when the hydroformylation was carried out using more than 3 mole equivalents of ligand per mole of rhodium.

(k) comparative run

EXAMPLE 4

The same procedure and conditions employed in Example 1 of preparing a rhodium catalytic precursor solution using rhodium dicarbonyl acetylacetonate. Texanol® and 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl)phosphite ligand and hydroformylating trans-butene-2 were repeated, save for the exceptions of employing various different olefins as the starting hydroformylation material and varying the rhodium complex catalyst precursor solutions and hydroformylation reaction conditions as shown in TABLE 4 below. The hydroformylation reaction rate in terms of gram moles per liter per hour of aldehyde produced as well as the mole ratio of linear aldehyde to branched aldehyde product were determined as in Example 1 and the results are given in TABLE 4 below.

TABLE 4

Olefin	[Rh] ppm	Ligand/Rh mole ratio	Partial Pressure CO (psia)	Partial Pressure H_2 (psia)	Olefin m moles or (MPa (psia))	Temp. °C	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
Butene-1	200	10	0.41 (60)	0.41 (60)	50	100	14.5	2.3
Butene-2 (trans)	250	10	0.21 (30)	0.21 (30)	50	100	6.63	0.77
Isobutene	150	10	0.10 (15)	0.31 (45)	50	115	1.65	a
Cyclohexene	150	10	0.41 (60)	0.41 (60)	63	100	4.8	b
Dicyclopentadiene	150	10	0.41 (60)	0.41 (60)	9.2	100	2.1	c
Vinyl Acetate	200	10	0.41 (60)	0.41 (60)	56	80	0.37	d
Allyl Alcohol	100	10	0.41 (60)	0.41 (60)	73.5	70	2.97	e
Allyl-tert-butyl ether	100	10	0.41 (60)	0.41 (60)	30	70	1.90	1.3
1,5-Hexadiene	100	10	0.41 (60)	0.41 (60)	43	70	2.11	2.5 f
Ethylene	100	10	0.14 (20)	0.14 (20)	(0.17 (25))	60	1.48	g
Ethylene	500	3	0.17 (25)	0.17 (25)	(0.17 (25))	30	0.27	g

(continued next page)

TABLE 4(continued)

Olefin	[Rh] ppm	Ligand/Rh mole ratio	Partial Pressure Olefin / H_2 / CO (psia)	Temp. °C	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
Propylene	500	3	0.17(25) 0.17(25) (0.17(25))	30	0.14	1.77
Cyclohexene	200	25	0.28(40) 0.28(40) 50	160	3.5	b
Decene-1	200	10	0.33 (47.5) (0.33 (47.5)) 22	100	5.7	1.1 h
Styrene	200	10	0.33 (47.5) (0.33 (47.5)) 30	100	10.0	1.9 i
Methyl methacrylate	200	10	0.33 (47.5) (0.33 (47.5)) 47	100	2.5	j

a-One product (3-methylbutyraldehyde) is formed.
b-One product (cyclohexane carboxaldehyde) is formed.
c-Several isomeric aldehydes are formed.
d-Only the branched isomer, α'-acetoxypropionaldehyde, is detected.
e-Only the linear isomer, 4-hydroxy-butyraldehyde is detected.
f-The ratio refers to that of the hept-6-ene-1-al and 2-methyl-hex-5-ene-1-al.
g-One product (propionaldehyde) is formed.
h-The ratio refers to that of n-undecanal and 2-methyldecanal.
i-The ratio refers to that of 3-phenylpropionaldehyde and 2-phenylpropionaldehyde.
j-One product [methyl (2-methyl-3 formyl) propionate] is formed.

EXAMPLE 5

The long term catalyst stability of 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite (the diorganophosphite ligand of Example 1) promoted rhodium catalyst as compared to diphenyl(2,6-di-tert-butyl-4-methylphenyl)phosphite (the triorganophosphite ligand of Run No. 2 in Table 3 above) promoted

rhodium catalyst was determined in the following manner.

These long term catalyst stability experiments were conducted by hydroformylating trans-butene-2 in a glass reactor in a continuous single pass mode. The reactor consisted of a 90 ml (three ounce) pressure bottle submersed in an oil bath with a glass front for viewing. In each experiment about 20 ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. Each precursor solution contained about 200 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 5 mole equivalents of phosphorous ligand per mole of rhodium metal and n-valeraldehyde trimer as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction in each experiment was conducted at a total gas pressure of about 1.24 MPa psig.) using about 0.21 MPa (30 psia.) hydrogen, about 0.17 MPa (24 psia.) trans-butene-2 and about 0.21 MPa (30 psia.) carbon monoxide, the remainder being nitrogen. The flows of the feed gases (carbon monoxide, hydrogen and propylene) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via stainless steel spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas was analyzed for C_5 aldehyde products periodically over four days of continuous operation at the reaction temperatures given in TABLE 5 below. The average reaction rates for each experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the n-valeraldehyde to 2-methylbutyraldehyde product ratio for each day of operation are given in TABLE 5 below.

TABLE 5

TEST RESULTS - DAILY AVERAGES

Ligand Used	Days Onstrm.	Temp. °C.	Rhodium PPM*	Ligand Wt.%	Partial Pressures CO MPa (psia)	Partial Pressures H_2 MPa (psia)	Trans butene-2 MPa (psia)	Reaction Rate Gram Moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio	Mole % Butene-1**
A	1.0	105	170	0.4	0.21 (31)	0.21 (30)	0.12 (18)	0.83	1.05	5.90
	1.9	105	167	0.3	0.21 (30)	0.20 (29)	0.16 (23)	1.09	1.08	6.04
	2.9	105	171	0.4	0.21 (30)	0.20(29)	0.15 (22)	1.05	1.09	5.92
	3.5	105	174	0.4	0.21 (30)	0.21 (31)	0.16 (23)	1.03	1.12	5.86
A	4.4	105	170	0.4	0.20(29)	0.21 (31)	0.17 (24)	1.06	1.11	5.84
B	1.0	105	177	0.4	0.21(30)	0.24(35)	0.18 (26)	0.36	0.74	5.57
	1.9	105	184	0.4	0.21(30)	0.19 (28)	0.23 (33)	0.26	0.69	4.98
	2.9	105	189	0.4	0.21(30)	0.20(29)	0.23 (34)	0.17	0.51	4.10
	3.5	105	192	0.4	0.20(29)	0.21 (31)	0.23 (34)	0.12	0.47	3.16
B	4.4	105	186	0.4	0.21(30)	0.21 (31)	0.23 (33)	0.09	0.48	2.56

A = 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite
B = diphenyl(2,6-di-tert-butyl-4-methylphenyl) phosphite
* Charging values reflect change in daily average liquid reactor solution levels.
** Percent of Isomerized Butene - 1 of the total amount of Butenes in the reactor outlet gas.

The above data show that the diorganophosphite ligand [1,1'-biphenyl-2,2'-diyl-(2, 6-di-tert-butyl-4-methylphenyl)phosphite] of this invention maintained catalytic activity after over four days of continuous hydroformylation whereas the comparative triorganophosphite ligand [diphenyl(2, 6-di-tert-butyl-4-methylphenyl)phosphite] promoted catalyst, which is not of this invention, lost about 75% of its catalytic actlvity over the same period of time. Analysis of the outlet gas composition indicated that total (equilibrium) isomerization of the pure butene-2 feed was achieved when the diorganophosphite (Ligand A) was

employed. The outlet butene-1 concentration (of the total butenes in the outlet) approximates the calculated thermodynamic equilibrium value of 5.77 mole percent of butene-1 at 105°C and a total pressure of 1.21 MPa (175 psia.). The triorganophosphite (Ligand B) showed an ability to isomerize butene-2, but this rapidly diminished over the period of the test.

EXAMPLE 6

A series of various rhodium complex catalyst precursor solutions consisting essentially of solubilized rhodium carbonyl diorganophosphite acetylacetonate complex precursor catalyst, organic solvent and free diorganophosphite ligand were prepared and employed to hydroformylate isobutylene into aldehyde in the following manner.

Rhodium dicarbonyl acetylacetonate was mixed with a sufficient amount of diorganophosphite ligand and diluted with sufficient solvent. Texanol®, to produce a rhodium catalytic precursor solution containing about 150 ppm of rhodium calculated as free metal and about 10 mole equivalents of diorganophosphite ligand per mole of rhodium. The ligand being varied as given in TABLE 6 below.

In each hydroformylation reaction, about 20 milliliters of the rhodium catalytic precursor solution so prepared was charged to the autoclave reactor described in Example 1 under nitrogen and heated to the reaction temperature employed as given in TABLE 6 below). The reactor was then pressurized to 0.17 MPa (10 psig.) with nitrogen and 5 ml (about 3.12 grams of isobutylene) introduced into the reactor. Then about 0.21 MPa (30 psia) hydrogen and about 0.21 MPa (30 psia.) of a 1:1 syn gas mixture (0.10 MPa (15 psia.) of carbon monoxide and 0.10 MPa (15 psia)of hydrogen) were introduced into the reactor via the gas manifold and the isobutylene so hydroformylated.

The hydroformylation reaction rate in gram moles per liter per hour of aldehyde produced (3-methylbutyraldehyde being the only aldehyde product) was determined from sequential 34.5 kPa (5 psia.) pressure drops in the reactor, spanning the nominal operating pressure in the reactor and the results are given in TABLE 6 below, said results being determined up to about a 30 percent conversion of the isobutylene starting material.

TABLE 6

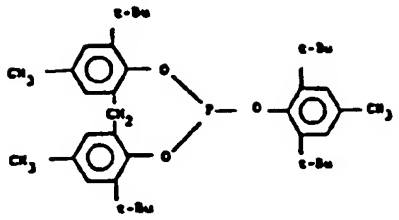
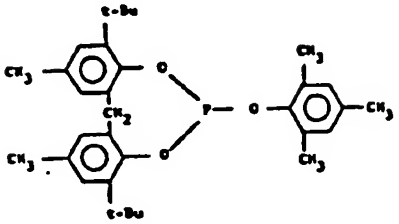
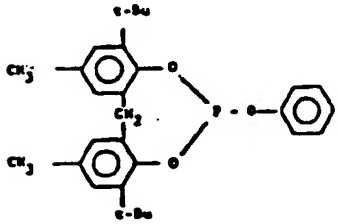
Run No.	Ligand	Temp. °C	Reaction Rate gram moles/ Liter/Hr.
1*		115	0.07
2		115	0.42
3		115	1.80
4	do.	100	1.50

TABLE 6 (continued)

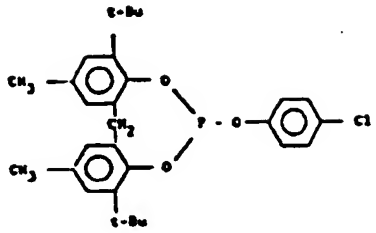
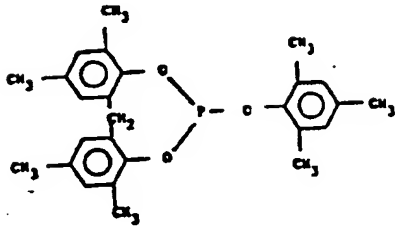
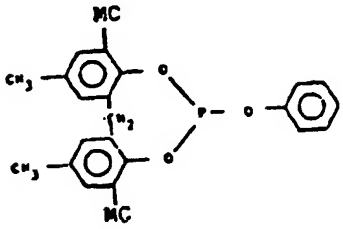
Run No.	Ligand	Temp. °C	Reaction Rate gram moles/ Liter/Hr.
5	do.	85	1.15
6		100	1.38
7		100	2.15
8		100	1.49

TABLE 6 (continued)

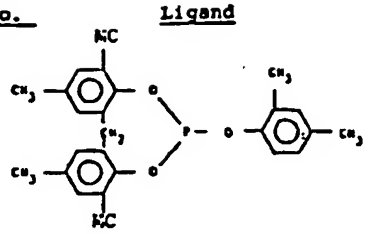
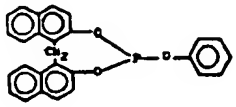
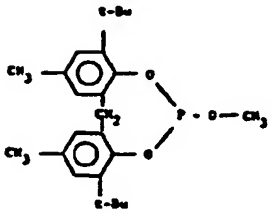
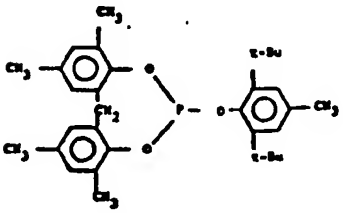
Run No.	Ligand	Temp. °C	Reaction Rate gram moles/ Liter/Hr.
9		100	1.92
10*		100	0.05
11		100	1.56
12		100	0.34

TABLE 6 (continued)

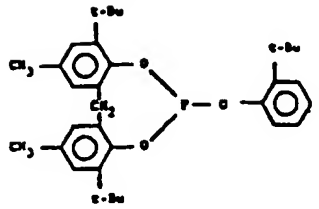
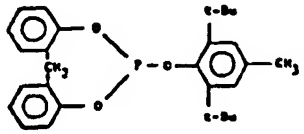
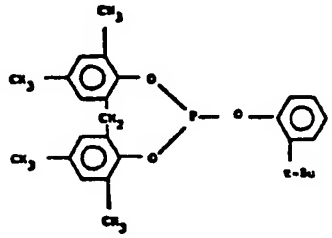
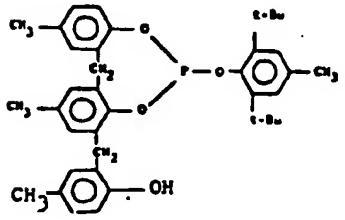
Run No.	Ligand	Temp. °C	Reaction Rate gram moles/ Liter/Hr.
13		100	0.86
14		100	3.25
15		100	0.40
16*		100	0.22

TABLE 6 (continued)

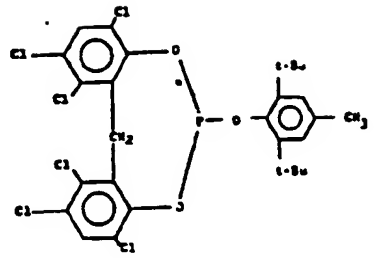
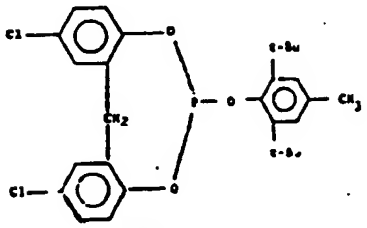
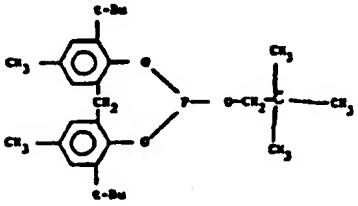
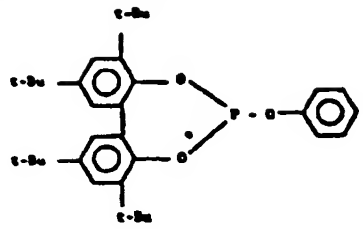
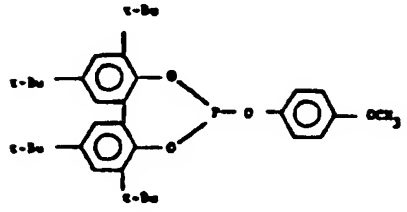
Run No.	Ligand	Temp. °C.	Reaction Rate gram moles/ Liter/Hr.
17*		100	0.05
18		100	1.29
19		100	1.25
20	do.	115	0.87

TABLE 6 (continued)

Run No.	Ligand	Temp. °C.	Reaction Rate gram moles/ Liter/Hr.
21		100	2.99
22		100	3.30

t-Bu = tertiary-Butyl
MC = 1-Methylcyclohexyl
* = Comparative run

EXAMPLE 7

A series of various rhodium complex catalyst precursor solutions consisting essentially of solubilized rhodium carbonyl diorganophosphite acetylacetonate complex precursor catalyst, organic solvent and free diorganophosphite ligand were prepared and employed to hydroformylate trans-butene-2 into C_5 aldehydes in the following manner.

Rhodium dicarbonyl acetylacetonate was mixed with a sufficient amount of a diorganophosphite ligand and diluted with sufficient solvent, Texanol®, to produce a rhodium catalytic precursor solution containing about 250 ppm of rhodium calculated as free metal and about 10 mole equivalents of diorganophosphite ligand per mole of rhodium. The ligand being varied as given in TABLE 7 below.

In each hydroformylation reaction, about 15 milliliters of the rhodium catalytic precursor solution so prepared was charged to the autoclave reactor under nitrogen and heated to the hydroformylation reaction temperature of 100° C. The reactor was then vented down to 0.13 MPa (5 psig.) and 5 ml (2.9 grams) of the olefin employed (as given in TABLE 7 below) introduced into the reactor. Then about 0.61 MPa (90 psia.) of a 1:1 syn gas mixture (0.31 MPa (45 psia.) of carbon monoxide and 0.31 MPa (45 psia) of hydrogen) were introduced into the reactor via the gas manifold and the olefin so hydroformylated.

The hydroformylation reaction rate in gram moles per liter per hour of C_5 aldehydes produced was determined from sequential 34.5 kPa (5 psia.) pressure drops in the reactor spanning the nominal operating pressure in the reactor, while the mole ratio of linear (n-valeraldebyde) to branched (2-methylbutyraldehyde) product was measured by gas chromatography and the results are given in TABLE 7 below, said results being determined after about a 5 to 20 percent conversion of the trans-butene-2 starting material.

TABLE 7

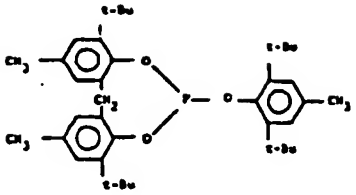
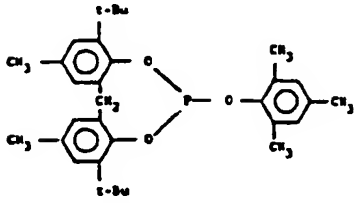
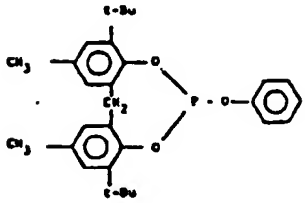
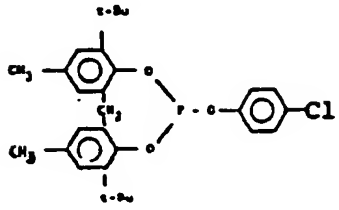
Run No.	Ligand	Reaction Rate Gram/Moles /Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
1*		0.0	-
2		2.8	0.72
3		7.0	0.62
4		8.1	0.67

TABLE 7 (continued)

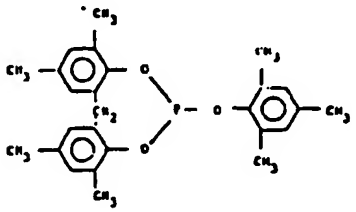
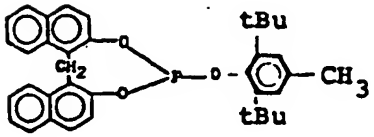
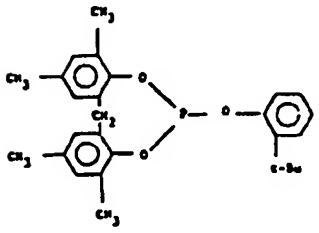
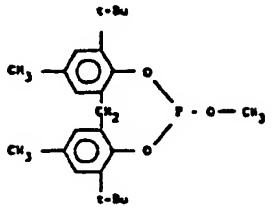
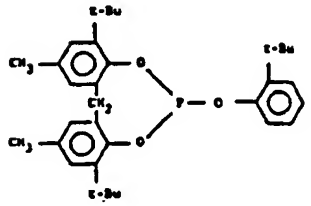
Run No.	Ligand	Reaction Rate Gram Moles /Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
5		12.0	0.78
6		12.0	0.93
7		1.9	1.2

TABLE 7 (continued)

Run No.	Ligand	Reaction Rate Gram Moles /Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
8		5.5	0.67
9		8.1	0.69

t-Bu = tertiary-Butyl ~~radical~~

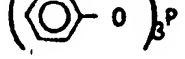
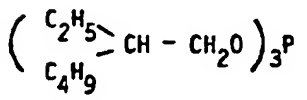
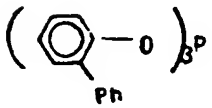
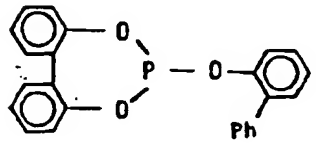
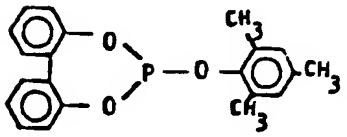
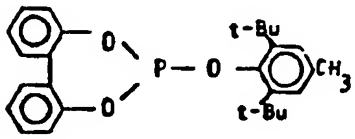
* = comparative run.

EXAMPLE 8

The reactivity of various diorganophosphite and triorganophosphite ligands towards aldehyde were determined as follows.

A series of phosphite-aldehyde solutions were prepared, each in the same manner, by successively charging, to an oven dried (150° C for one hour) 60 ml (2.0 -oz.) narrow-neck bottle which had cooled to ambient temperature in a dry box and which contained a magnetic stirring bar, about 4.5 m moles of phosphite ligand, about 3.0 m moles of triphenyl phosphine oxide, as a phosphorus containing internal standard, and a sufficient amount of a mixture of n-valeraldehyde and 2-methylbutyraldehyde to obtain a combined weight of 30 grams for each solution. The bottle was then sealed with a serum stopper, removed from the dry box and placed on a magnetic stirrer at ambient temperature until a solution was obtained. The bottle was then returned to the dry box to remain under nitrogen atmosphere at ambient temperature. Periodically 3 milliliter samples of each solution were drawn and the phosphite concentration analyzed by phosphorus-31 NMR spectroscopy. The extent of phosphite decomposition (as a result of reacting with aldehyde) was qualitatively determined from the relative intensities of the ^{31}P NMR resonances corresponding to those of the pure phosphite ligand employed and the internal standard. The phosphite ligands employed and the test results are given in TABLE 8 below.

TABLE 8

Run No.	Ligand Structure	Extent of Phosphite Decomposition			
		Day 1	Day 4	Day 7	Day 10
1.		Some	All	-	-
2.		Some	Most	-	-
3.		None	Some	Most	All
4.		All	-	-	-
5.		Some	Most	-	-
6.		None	None	None	None

t-Bu = tertiary Butyl
Ph = Phenyl

EXAMPLE 9

The reactivity of various phosphite ligands towards aldehyde at high temperatures were determined as follows.

A series of phosphite-aldehyde solutions were prepared, each in the same manner by successively charging a 360 ml (12 -oz.) Fischer-Porter bottle containing a magnetic stirring bar, with about 0.005 moles of phosphite ligand, about 0.0075 moles of barium carbonate, about 0.0025 moles of barium valerate (the barium salts being employed to maintain neutrality of the solution) and a sufficient amount of a mixture of n-valeraldehyde and 2-methylbutyraldehyde to obtain a combined weight of 100 grams for each solution. The bottle was sealed with a pressure cap modified to contain a mechanical stirrer and gas purging and sampling valves and inserted into a stainless steel wire mesh protective covering. The bottle containing the

phosphite-aldehyde solution was then purged with nitrogen and about 0.45 MPa 50 psig nitrogen allowed to remain. Each solution was then stirred for one hour at ambient temperature. Each phosphite-ligand solution was then heated by placing the bottle into a preheated (160 °C) silicone oil bath. Periodically samples of each solution were withdrawn and the phosphite concentration determined quantitatively by high pressure liquid chromatography. The phosphite ligands employed and extent of phosphite decomposition (as a result of reacting with the aldehyde) are given in TABLE 9 below.

TABLE 9

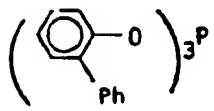
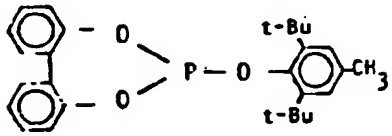
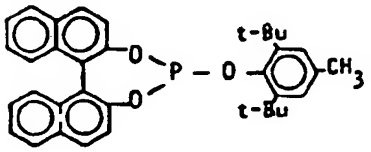
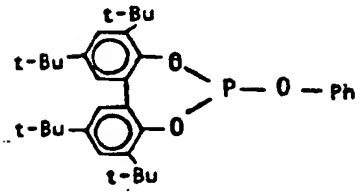
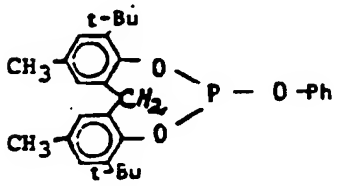
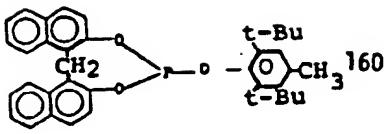
Run No.	Ligand	°C	Reaction Time (hrs)	Percent Ligand Decomposed
1		160	23.5	44
2		160	21	13
3		160	25	0
4		160	21	4
5		160	21	4

TABLE 9 (CONT.)

Run No.	Ligand	Temp °C	Reaction Time (hrs)	Percent Ligand Decomposed
6		160	25	0.5

t-Bu = tertiary-Butyl
Ph = Phenyl

EXAMPLE 10

In a continuous catalyst liquid recycle manner, a mixed olefin starting material of butene-1 and butene-2 (cis and trans) was hydroformylated for six days followed by the continuous catalyst liquid recycle hydroformylation of butene-1 as follows.

The liquid recycle reactor system employed contained two 2.8 liter stainless steel stirred tank reactors, connected in series, each containing a vertically mounted agitator and a circular tubular sparger near the bottom of the reactor for feeding the olefin and/or syn gas. The sparger contained a plurality of holes of sufficient size to provide the desired gas flow into the liquid body. Reactor 1 contained a silicone oil shell as means of bringing the contents of the reactors up to reaction temperature while the reaction solution in Reactor 2 was heated by an electrical heater. Both reactors contained internal cooling coils for controlling the reaction temperature. Reactors 1 and 2 were connected via a line to transfer any unreacted gases from reactor 1 to reactor 2 and were further connected via a line so that a portion of the liquid reaction solution containing aldehyde product and catalyst from reactor 1 could be pumped into reactor 2 wherein the unreacted olefin of reactor 1 is further hydroformylated in reactor 2.

Each reactor also contained a pneumatic liquid level controller for automatic control of the liquid levels in the reactors. Reactor 1 further contained a line for introducing the olefin and syn gas through the sparger, while make up syn gas was added to reactor 2 via the same transfer line carrying the unreacted gases from reactor 1. Reactor 2 also contained a blow-off vent for removal of the unreacted gases. A line from the bottom of reactor 2 was connected to the top of a vaporizer so that a portion of the liquid reaction solution could be pumped from reactor 2 to the vaporizer. Vaporized aldehyde was disengaged from the non-volatilized components of the liquid reaction solution in the gas-liquid separator part of the vaporizer. The remaining non-volatilized catalyst containing liquid reaction solution was pumped through a recycle line back into reactor 1. The recycle line also contained a pneumatic liquid level controller. The vaporized aldehyde product was passed into a water-cooled condenser, liquified and collected in a product receiver.

The hydroformylation reaction was conducted by charging about 0.789 liters of a catalyst precursor solution of rhodium dicarbonyl acetylacetonate (about 200 ppm rhodium), about 1.0 wt. % 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4 -methylphenyl)phosphite ligand (about 10 mole equivalents of ligand per mole of rhodium), about 0.5 wt. % 2,6-di-tert-butyl-4-methylphenol as an antioxidant, and about 98.5 wt. % of C_5 aldehyde (about 68.5 wt % valeraldehyde and about 30 wt % valeraldehyde trimer) as solvent to reactor 1. About 0.96 liters of the same catalyst precursor solution was charged to reactor 2. The reactor system was then purged with nitrogen to remove any oxygen present. Then about 0.79 MPa (100 psig.) nitrogen

pressure was put on both reactors and the reactors heated to their reaction temperatures given in TABLE 10 below. Controlled flows of purified hydrogen, carbon monoxide and a mixed olefin starting material of butene-1 and butene-2 (cis and trans) were fed through the sparger into the bottom of reactor 1 and the reactor pressure increased to the operating pressure given in TABLE 10 below. When the liquid level in reactor 1 started to increase as a result of liquid aldehyde product formation a portion of the liquid reaction solution of reactor 1 was pumped into reactor 2 through a line into the top of reactor 2 at a rate sufficient to maintain a constant liquid level in reactor 1. The pressure of reactor 2 increased to its operating pressure given in TABLE 10 below. Blow-off gas from reactor 2 was analyzed and measured. A controlled flow of make-up syn gas (CO and H_2) was added to reactor 2 in order to maintain their desired partial pressures in reactor 2. The operating pressures and reaction temperatures were maintained throughout the hydroformylation. As the liquid level in reactor 2 started to increase as a result of liquid aldehyde product formation, a portion of the liquid reaction solution was pumped to the vaporizer/separator at a rate sufficient to maintain a constant liquid level in reactor 2. The crude aldehyde product was separated at 115°C and 0.14 MPa (20 psia.) from the liquid reaction solution, condensed and collected in a product receiver. The remaining non-volatilized catalyst containing liquid reaction solution was recycled back to reactor 1.

The hydroformylation of said mixed olefin feed of butene-1 and butene-2 was carried out continuously for six days after which time the olefin feed was changed over to a predominately butene-1 feed and continued for an additional day.

The hydroformylation reaction conditions as well as the rate of C_5 aldehydes produced in terms of gram moles per liter per hour and the linear to branched aldehyde product ratio of n-valeraldehyde to 2-methylbutyraldehyde are given in TABLE 10 below.

TABLE 10

Days of Operation	2	6	7
Butene Feed, mol %			
Butene-1	5.22	41.27	99.97
Trans-Butene-2	57.00	34.06	0.0
Cis-Butene-2	37.78	24.67	0.03
Reactor No. 1			
Temperature, °C	85.2	85.4	66.1
Pressure, (psia) MPa	1.41 (205)	1.41 (205)	1.41 (205)
H_2, (psia) MPa	0.594 (86.3)	0.442 (64.2)	0.535 (78.3)
CO, (psia) MPa	0.439 (63.7)	0.434 (63.1)	0.523 (75.9)
Butene-1, (psia) MPa	0.005 (0.7)	0.010 (1.5)	0.174 (25.3)
Trans-Butene 2, (psia) MPa	0.158 (23.0)	0.127 (18.5)	0.008 (1.1)
Cis-Butene-2, (psia) MPa	0.050 (7.3)	0.049 (7.1)	0.012 (1.7)
Reactor No. 2			
Temperature, °C	85.1	85.5	68.5
Pressure, (psia) MPa	1.27 (185)	1.27 (185)	1.27 (185)
H_2, (psia) MPa	0.577 (83.8)	0.380 (55.1)	0.375 (54.4)
CO, (psia) MPa	0.261 (37.9)	0.378 (54.8)	0.358 (52.0)
Butene-1, (psia) MPa	0.003 (0.5)	0.002 (0.3)	0.048 (7.0)
Trans-Butene-2, (psia) MPa	0.112 (16.2)	0.076 (11.0)	0.014 (2.1)
Cis-Butene-2, (psia) MPa	0.026 (3.8)	0.020 (2.9)	0.019 (2.8)
Results			
C_5 Aldehydes, gmol/l/hr	3.03	3.19	3.19
Linear/Branched Aldehyde Ratio	0.47	0.78	2.44

Subsequent analysis of the rhodium complex catalyst solution after completion of the above continuous seven day hydroformylation experiment showed said used catalyst solution to contain about 173 ppm rhodium.

A comparable experiment was conducted employing a similar procedure as described in Example 10 above, but wherein the crude aldehyde product was separated at vaporizer conditions of about 87 to 89°C and about 34.5 kPa (5 psia.) from the liquid reactor solution and wherein the recycled catalyst containing solution was passed through an Amberlyst® A-21 bed to remove acidic by-products. After an equilibration

period of one day wherein some rhodium was believed to be adsorbed onto the Amberlyst® resin bed there were no detectable losses of rhodium inventory in the reactor over the next 10 days of continuous hydroformylation.

EXAMPLE 11

A similar continuous hydroformylation comparative experiment as set forth in Example 10 was carried out using tris-ortho-biphenylylphosphite, (Run No. 3 of TABLE 8, a phosphite not of this invention) as the ligand promoter. The start-up and operating procedure set forth in Example 10 were employed with the exception that in this test only a single reactor (in place of two reactors in series) was used with butene-1 as the olefin feed. The reactor was charged with 0.88 liters of a catalyst composition consisting of 100 ppm rhodium as rhodium dicarbonyl acetylacetonate, 10 wt% tris-orthobiphenylylphosphite (about 192 mole equivalents of phosphite ligand per mole equivalent of rhodium) dissolved in a 1:1 weight:weight mixture of valeraldehyde and Texanol®. At the end of 0.8 days of operation massive percipitation of alpha-hydroxypentyl phosphonic acid occurred which caused plugging of the reactor transfer lines and subsequent shut-down of the continuous hydroformylation. Analysis of the catalyst solution by Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy, showed that all tris-ortho-biphenylylphosphite had decomposed. The hydroformylation test was terminated. The data set forth in Table II below describes the operating conditions and performance prior to the forced shut-down of the process.

TABLE 11

Days of operation	**0.8**
Butene Feed, mole %	
Butene-1	**99.2**
Trans-Butene-2	**0.2**
Cis-Butene-2	**0.05**
Butane	**0.55**
Reaction Conditions	
Temperature, °C	**80.3**
Pressure, (psia) MPa	*1.033* **(150.0)**
H_2, (psia) MPa	*0.223* **(32.3)**
CO, (psia) MPa	*0.301* **(43.7)**
Butene-1 (psia) MPa	*0.418* **(60.6)**
Results	
C_5 Aldehydes Reaction Rate (gmoles/liter/hour)	**1.02**
Linear/Branched Aldehyde Mole Ratio	**3.04**

EXAMPLE 12

The long term catalyst stability of 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite promoted rhodium catalyst was determined in the following manner.

The hydroformylation was conducted in a glass reactor operating in a continuous single pass propylene hydroformylation mode. The reactor consisted of a 90 ml (three-ounce) pressure bottle submersed in an oil bath with a glass front for viewing. About 20-ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe,after purging the system with nitrogen. The precursor solution contained about 200 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 10 mole equivalents of 1,1'-biphenyl-2,2'-diyl-(2,6 -di-tert-butyl-4-methylphenyl)phosphite ligand per mole of rhodium metal and Texanol® as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures

of hydrogen, carbon monoxide, and propylene being given in Table 12 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen, propylene and nitrogen) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_4 aldehydes and the outlet gas analyzed over 22 days of continuous operation at the reaction temperature are given in TABLE 12 below. The average reaction rates for each experiment in terms of gram moles per liter per hour of product C_4 aldehydes as well as the n-butyraldehyde to iso-butyraldehyde product ratio are given in TABLE 12 below.

TABLE 12

TEST RESULTS - DAILY AVERAGES

Days Opern.	Temp. °C.	Rhodium PPM*	Ligand Wt.%	Partial Pressures CO MPa (psia)	Partial Pressures H_2 MPa (psia)	Partial Pressures Propylene MPa (psia)	Reaction Rate gram moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
0.6	73	132	0.7	0.14 (21)	0.25 (36)	0.03 (5)	1.09	0.86
1.4	91	159	0.8	0.25 (37)	0.34 (50)	0.04 (6)	2.62	1.02
2.6	91	145	0.7	0.23 (33)	0.29 (42)	0.05 (7)	2.40	1.01
3.9	91	135	0.7	0.28 (41)	0.37 (53)	0.03 (4)	2.22	1.04
4.9	91	126	0.6	0.27 (39)	0.34 (50)	0.03 (4)	2.24	1.01
4.5	91	136	0.7	0.26 (38)	0.34 (50)	0.03 (5)	2.37	1.06
6.7	91	173	0.9	0.28 (40)	0.35 (51)	0.04 (6)	2.39	1.08
7.7	91	179	0.9	0.28 (41)	0.37 (53)	0.05 (7)	2.12	1.03
7.1	91	188	0.9	0.29 (42)	0.41 (60)	0.06 (9)	1.93	0.90
9.6	91	198	1.0	0.29 (42)	0.36 (52)	0.04 (6)	2.10	1.06
11.0	91	197	1.0	0.28 (41)	0.34 (50)	0.05 (7)	2.42	1.07
12.0	91	197	1.0	0.14 (21)	0.53 (85)	0.13 (19)	0.94	0.36
12.6	91	197	1.0	0.28 (41)	0.34 (50)	0.06 (8)	2.35	1.06

TABLE 12 (Continued)

TEST RESULTS - DAILY AVERAGES

Days Operation	Temp. °C.	Rhodium PPM*	Ligand Wt.%	Partial Pressures CO (psia)	Partial Pressures H_2 (psia)	Propylene (psia)	Reaction Rate gram moles/ Liter/Hour	Linear/ Branched Aldehyde Mole Ratio
13.7	89	205	1.1	0.26(39)	0.57 (86)	0.10 (14)	1.86	0.77
14.7	88	209	1.1	0.28(41)	0.34(50)	0.06 (9)	2.56	1.09
15.6	101	214	1.1	0.29(42)	0.34(50)	0.06 (9)	2.40	1.05
16.9	91	199	1.0	0.28(40)	0.34(50)	0.06 (8)	2.46	1.08
17.9	91	200	1.0	0.28(41)	0.34 (50)	0.06 (8)	2.46	1.07
18.9	91	202	1.0	0.28(41)	0.34(50)	0.06 (9)	2.38	1.07
19.6	91	204	1.0	0.27(40)	0.34(50)	0.06 (9)	2.48	1.07
22.5	92	209	1.0	0.29(42)	0.34(50)	0.06 (8)	2.34	1.08

* Changing values reflect change in daily liquid reactor solution levels

EXAMPLE 13

A similar continuous hydroformylation experiment as set forth in Example 10 was carried out using isobutylene as the olefin and phenyl [2,2'-methylene-bis(6-t-butyl-4-methylphenyl)] phosphite (the ligand in Run No. 3 of Table 6) as the ligand promoter. The start-up and operating procedure set forth in Example 10 were employed with the exception that only a single reactor (in place of the two reactors in series) was used with isobutylene as the olefin feed and the above mentioned phosphite as the ligand. The reactor was charged with 1127 ml. of a catalyst composition consisting of 200 ppm rhodium as rhodium dicarbonyl acetylacetonate, 0.9 wt. % of phenyl [2,2' methylene-bis(6-t-butyl-4-methylphenyl)] phosphite (about 10 mole equivalents of phosphite ligand per mole equivalent of rhodium) dissolved in a mixture of about 475 gr. of valeraldehyde and about 466 gr. of Texanol.® The data set forth in Table 13 below describes the operating conditions and performance in gram moles per liter per hour of 3-methylbutyraldehyde product

over three days of continuous hydroformylation.

TABLE 13

Days of Operation	1	2	3
Olefin Feed Mole %			
Isobutylene	99.96	99.94	100
Isobutane	0.04	0.06	-
Reaction Conditions			
Temperature, °C.	84.8	84.8	84.8
Pressure, (psia) MPa	1.38 (201)	1.41 (204)	1.42 (206)
H_2, (psia) MPa	0.509 (73.92)	0.521 (75.65)	0.453 (65.76)
CO, (psia) MPa	0.023 (3.34)	0.055 (7.98)	0.287 (41.64)
Isobutylene, (psia) MPa	0.730 (106.0)	0.677 (98.24)	0.590 (85.59)
Results			
3-Methylbutyraldehyde	1.55	1.60	0.64
Reaction Rate (g moles/liter/hour)			

EXAMPLE 14

Butene-2 was hydroformylated in the same manner as Example 12 using 1,1'-binaphthylene-2,2'-diyl-(2,6-di-t-butyl-4-methylphenyl) phosphite as the ligand, (the ligand of Run No. 9 of Table 3).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass butene-2 hydroformylation mode. The reactor consisted of a 90 ml (three ounce) pressure bottle submersed in an oil bath with a glass front for viewing. About 20 ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 200 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 9.6 mole equivalents of 1,1'-binaphthylene-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite ligand per mole of rhodium metal and Texanol® as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and butene-2 being given in Table 14 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and butene-2) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution

via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas analyzed over about 14 days of continuous operation at the reaction temperatures are given in TABLE 14 below. The average reaction rates for each experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the linear n-valeraldehyde to 2-methylbutyraldehyde branched product ratio are given in TABLE 14 below.

TABLE 14

TEST RESULTS - DAILY AVERAGES

Days On Exp.	Temp. °C.	Rhodium ppm*	Ligand wt.%*	Partial Pressures			Reaction Rate gram moles/ Liter/Hour	Linear/Branched Aldehyde Mole Ratio
				CO H_2(psia)	H_2 H_2(psia)	Butene-2 H_2(psia)		
0.8	102	146	0.7	0.29(42)	0.33(48)	0.12 (18)	1.10	0.20
1.6	100	162	0.8	0.22(32)	0.27(39)	0.15 (22)	1.52	1.30
2.2	100	163	0.8	0.23(34)	0.28(41)	0.17 (24)	1.74	1.20
3.8	100	153	0.8	0.23 (34)	0.34(49)	0.17(25)	1.79	1.07
4.5	100	156	0.8	0.22 (32)	0.27(39)	0.16 (23)	1.74	1.18
4.6	100	186	0.9	0.23 (33)	0.28 (40)	0.17 (24)	1.68	1.36
6.7	100	223	1.1	0.23 (33)	0.28(40)	0.17 (25)	1.73	1.39
7.7	100	86	0.4	0.21 (30)	0.25(37)	0.15 (22)	1.06	0.84
7.1	100	171	0.9	0.23 (34)	0.28(40)	0.24 (35)	1.80	1.09
10.7	100	189	1.9	0.23 (34)	0.27(39)	0.25 (36)	1.85	1.19
11.8	110	183	1.9	0.24 (35)	0.28(41)	0.24 (35)	1.86	1.00
12.8	110	215	1.1	0.24 (35)	0.28(41)	0.25 (37)	2.08	1.12
13.6	110	260	1.3	0.25 (36)	0.29(42)	0.26 (38)	1.76	1.28

* Changing values reflect changes in daily liquid reactor solution levels.

EXAMPLE 15

Isobutylene was hydroformylated in the same manner as Example 12 using 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite as the ligand (the ligand of Example 1).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass isobutylene hydroformylation mode. The reactor consisted of a 90 ml (three ounce)pressure bottle submersed in an oil bath with a glass front for viewing. About 20 ml of a freshly prepared rhodium catalytic

precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 250 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 10 mole equivalents of 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4-methylphenyl) phosphite ligand per mole of rhodium metal and Texanol® as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and isobutylene being given in Table 15 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and isobutylene) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the 3-methylbutyraldehyde product and the outlet gas analyzed over 7 days of continuous operation at the reaction temperatures are given in TABLE 15 below. The average reaction rates for each experiment in terms of gram moles per liter per hour of 3-methylbutyraldehyde product is given in Table 15 below.

TABLE 15

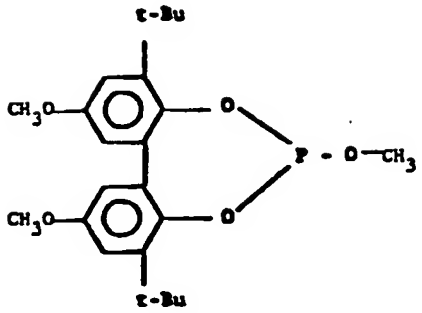
TEST RESULTS - DAILY AVERAGES

Days Operm.	Temp. °C.	Rhodium ppm*	Ligand wt.%*	Partial Pressures CO (psia)	H_2 (psia)	Isobutylene H_2(psia)	Reaction Rate gram moles/ Liter/Hour
0.8	99	179	0.8	0.22 (32)	0.48 (69)	0.19 (27)	1.09
1.7	115	252	1.1	0.21 (31)	0.59 (85)	0.35 (51)	1.46
2.7	115	226	1.0	0.18 (26)	0.18 (26)	0.46 (96)	1.54
3.1	115	207	0.9	0.57 (83)	0.51 (74)	0.08 (11)	1.48
5.8	115	279	1.2	0.48 (70)	0.50 (73)	0.18 (26)	0.68
6.6	115	205	0.9	0.50 (72)	0.49 (71)	0.18 (26)	0.58
7.1	115	210	0.9	0.43 (63)	0.43 (62)	0.30 (43)	0.84

* Changing values reflect change in daily liquid reactor solution levels

EXAMPLE 16

Methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite having the formula



was prepared in the following manner.

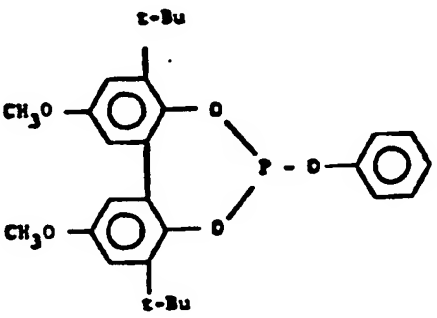
A solution of about 90 grams (about 0.5 moles) of 2-t-butyl-4-methoxyphenol and 170 ml. of H_2O containing about 56 grams (about 1.0 mole) of potassium hydroxide was heated with stirring to about 80°C. Air was then passed through the solution until precipitation of a diphenolic compound (i.e. 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl) was complete (total reaction time of about 135 minutes). The white, solid diphenolic precipitate was then filtered hot and washed twice with about 200 ml of water. About 78 grams (87.6 % of theory) of the isolated 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl product was recovered which had a melting point of about 222 to 224°C and whose structure was confirmed by infrared and mass spectroscopy.

About 75.2 grams of the 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl diol so prepared was then added to about 1 liter of toluene. Sufficient toluene was then removed azeotropically to remove residual traces of moisture from the solution. The diol-toluene solution was then cooled to 0°C and about 70 grams of triethylamine added followed by the dropwise addition of about 29 grams of phosphorus trichloride at 0°C over about 20 minutes. The reaction solution became thick with triethylamine hydrochloride salt and was heated for about 30 minutes at about 100°C. The suspension was then cooled to about 55°C and about 13.44 grams of methanol added over about 15 minutes and the reaction medium heated at about 90 to 95°C for about one hour. The reaction medium was then filtered hot to remove the solid triethylamine hydrochloride precipitate and the filtrate evaporated to dryness under vacuum. The recovered residue was then dissolved in about 100 ml of refluxing acetonitrile and cooled to precipitate the desired methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand, about 75 grams (85.4% yield of theory) of which was recovered. The desired crystalline, solid phosphite ligand product was found to have a melting point of about 64 to 69°C and a characteristic ^{31}P NMR phosphite resonance at 131.9 ppm (relative to external H_3PO_4).

EXAMPLE 17

The following diorganophosphite ligands were prepared in the same manner as described in Example 16 above, save of course for employing the hydroxy compound reactants that correspond to and account for their diorganophosphite structures.

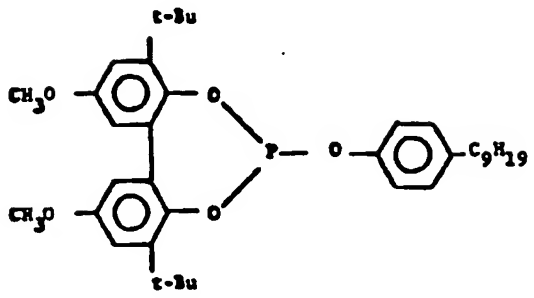
Ligand A



phenyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite. (Crystalline product having a melting point of 131 to 132°C and having a characteristic ^{31}P NMR phosphite resonance at 140.1 ppm,

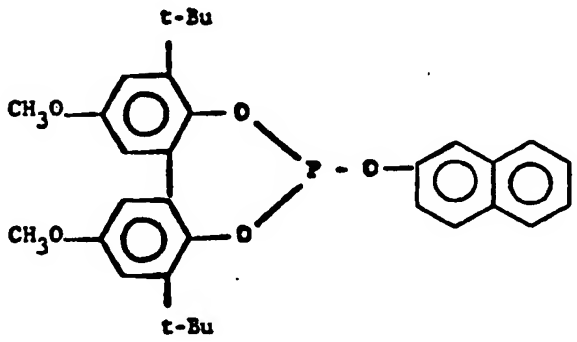
relative to external H_3PO_4)

Ligand B



4-nonylphenyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite (Non-crystalline gum product having characteristic ^{31}P NMR phosphite resonances at 140.1 ppm and 139.9 ppm, relative to external H_3PO_4; "nonyl" represents branched mixed nonyl radicals).

Ligand C



beta-naphthyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite (Non-crystalline gum product having a characteristic ^{31}P NMR phosphite resonance at 139.2 ppm, relative to external H_3PO_4).

EXAMPLE 18

Butene-2 was hydroformylated in the same manner as in Example 12 using methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite as the ligand, (the ligand of Example 16).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass butene-2 hydroformylation mode. The reactor consisted of a 90 ml (three ounce) pressure bottle submersed in an oil bath with a glass front for viewing. About 20 ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 250 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 2.0 weight percent ligand (about 19.7 mole equivalents of methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand per mole of rhodium metal) and valeraldehyde trimer as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and butene-2 being given in Table 16 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and butene-2) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas analyzed over about 11 days of continuous

operation at the reaction temperature of about 90°C are given in TABLE 16 below. The average reaction rates for this experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the linear n-valeraldehyde to 2-methylbutyraldehyde branched product ratio are given in TABLE 16 below.

TABLE 16

TEST RESULTS - DAILY AVERAGES

Days Operm.	Temp. °C.	Partial Pressures			Reaction Rate gram moles/ Liter/Hour	Linear/Branched Aldehyde Mole Ratio
		CO Hfa (psia)	H_2 Hfa (psia)	Butene-2 Hfa (psia)		
0.5	90	0.18 (26)	0.50 (72)	0.07 (10)	0.7	0.3
3.5	90	0.14 (20)	0.41 (59)	0.08 (12)	1.7	0.7
4.5	90	0.14 (20)	0.41 (60)	0.07 (10)	1.5	0.6
5.5	90	0.14 (20)	0.41 (60)	0.07 (10)	1.5	0.6
6.5	90	0.14 (20)	0.41 (60)	0.07 (10)	1.7	0.6
7.5	90	0.14 (21)	0.41 (60)	0.06 (8)	1.5	0.7
10.5	90	0.14 (20)	0.41 (60)	0.07 (10)	1.6	0.6
10.9	90	0.14 (20)	0.40 (58)	0.08 (12)	1.9	0.7

EXAMPLE 19

Butene-2 was hydroformylated in the same manner as in Example 12 using phenyl [3,3'-di-t-butyl-5,5'dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite as the ligand, (Ligand A of Example 17).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass butene-2 hydroformylation mode. The reactor consisted of a 90 ml (three ounce)pressure bottle submersed in an oil bath with a glass front for viewing. About 20 ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 250 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 2.0 weight percent ligand (about 17.2 mole equivalents of phenyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand per mole of rhodium metal) and valeraldehyde trimer as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and butene-2 being given in Table 17 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and butene-2) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas analyzed over about 13 days of continuous operation at the reaction temperature of about 90°C are given in TABLE 17 below. The average reaction rates for this experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the linear n-valeraldehyde to 2-methylbutyraldehyde branched product ratio are given in TABLE 17 below. Analysis after 2.5 days of operation indicated poor butene-2 feed due to plugging of the sparger. The problem was corrected and the reaction continued.

TABLE 17

TEST RESULTS - DAILY AVERAGES

Days Operm.	Temp. °C.	Partial Pressures			Reaction Rate gram moles/ Liter/Hour	Linear/Branched Aldehyde Mole Ratio
		CO	H_2	Butene-2		
		H_2 (psia)	H_2 (psia)	H_2 (psia)		
0.5	90	0.16 (23)	0.45 (65)	0.07 (10)	1.4	0.7
1.5	90	0.14 (20)	0.41 (60)	0.06 (9)	1.8	0.8
2.5	90	0.30 (43)	0.04 (6)	0.007 (1)	0.04	-
5.5	90	0.14 (21)	0.41 (59)	0.10 (14)	1.8	0.8
6.5	90	0.14 (21)	0.41 (59)	0.09 (13)	2.0	0.8
7.5	90	0.14 (21)	0.41 (60)	0.08 (12)	1.8	0.7
8.5	90	0.15 (22)	0.41 (60)	0.08 (12)	1.9	0.7
9.5	90	0.15 (22)	0.41 (60)	0.07 (10)	1.8	0.7
12.5	90	0.14 (21)	0.41 (60)	0.08 (12)	1.8	0.7
12.9	90	0.14 (21)	0.41 (60)	0.09 (13)	1.7	0.7

EXAMPLE 20

Butene-2 was hydroformylated in the same manner as in Example 12 using 4-nonyl [3,3'-di-t-butyl,-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite as the ligand, (Ligand B of Example 17).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass butene-2 hydroformylation mode. The reactor consisted of a 90 ml (three ounce) pressure bottle submersed in an oil

bath with a glass front for viewing. About 20 mℓ of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 250 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 2.0 weight percent ligand (about 13.6 mole equivalents of 4-nonyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand per mole of rhodium metal) and valeraldehyde trimer as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and butene-2 being given in Table 18 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and butene-2) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas analyzed over about 13 days of continuous operation at the reaction temperature of about 90°C are given in TABLE 18 below. The average reaction rates for this experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the linear n-valeraldehyde to 2-methylbutyraldehyde branched product ratio are given in TABLE 18 below.

TABLE 18

TEST RESULTS - DAILY AVERAGES

Days Oper.	Temp. °C.	Partial Pressures				Reaction Rate gram moles/ Liter/Hour	Linear/Branched Aldehyde Mole Ratio
		H_2 (psia)	CO (psia)	H_2 (psia)	Butene-2 (psia)		
0.5	90	0.14 (20)	0.41 (60)	0.16 (15)		1.0	0.7
1.5	90	0.11 (16)	0.48 (70)	0.08 (12)		1.2	1.0
2.5	90	0.10 (15)	0.48 (70)	0.16 (15)		1.5	1.0
5.5	90	0.11 (16)	0.47 (68)	0.10 (15)		1.7	1.5
6.5	90	0.11 (16)	0.48 (69)	0.10 (14)		1.8	1.5
7.5	90	0.12 (17)	0.48 (70)	0.08 (12)		1.7	1.5
8.5	90	0.11 (16)	0.48 (70)	0.07 (13)		1.8	1.5
9.5	90	0.12 (17)	0.48 (70)	0.08 (12)		1.6	1.5
12.5	90	0.11 (16)	0.48 (70)	0.10 (14)		1.7	1.6
12.9	90	0.11 (16)	0.48 (70)	0.09 (13)		1.5	1.7

EXAMPLE 21

A similar continuous hydroformylation experiment as set forth in Example 10 was carried out using isobutylene as the olefin and methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite (the ligand of Example 16) as the ligand promoter. The start-up and operating procedure set forth in Example 10 was employed.

The hydroformylation reaction was conducted by charging about 1.03 liters of a catalyst precursor solution of rhodium dicarbonyl acetylacetonate (about 450 ppm rhodium), about 2.8 wt.% methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl) phosphite ligand (about 15.3 mole equivalents of ligand per

mole of rhodium), about 2.0 wt.% triphenylphosphine oxide as an internal standard, and about 95.8 wt. % of C_5 aldehyde (about 82.8 wt % valeraldehyde and about 13.0 wt % valeraldehyde trimer) as solvent to reactor 1. About 1.2 liters of the same catalyst precursor solution was charged to reactor 2. The reactor system was then purged with nitrogen to remove any oxygen present. Then about 0.79 MPa (100 psig.) nitrogen pressure was put on both reactors and the reactors were heated to their reaction temperatures given in TABLE 19 below. Controlled flows of purified hydrogen, carbon monoxide and isobutylene (the composition of the isobutylene feed throughout this process consisted of at least 99.9 mole % or greater of isobutylene, any remainder being isobutane) were fed through the sparger into the bottom of reactor 1 and the reactor pressure increased to the operating pressure given in TABLE 19 below. When the liquid level in reactor 1 started to increase as a result of liquid aldehyde product formation a portion of the liquid reaction solution of reactor 1 was pumped into reactor 2 through a line into the top of reactor 2 at a rate sufficient to maintain a constant liquid level in reactor 1. The pressure of reactor 2 increased to its operating pressure given in TABLE 19 below. Blow-off gas from reactor 2 was analyzed and measured. A controlled flow of make-up syn gas (CO and H_2) was added to reactor 2 in order to maintain their desired partial pressures in reactor 2. The operating pressures and reaction temperatures were maintained throughout the hydroformylation. As the liquid level in reactor 2 started to increase as a result of liquid aldehyde product formation, a portion of the liquid reaction solution was pumped to the vaporizer/separator at a rate sufficient to maintain a constant liquid level in reactor 2. The crude aldehyde product was separated (at varying temperatures) from the liquid reaction solution, condensed and collected in a product receiver. The remaining non-volatilized catalyst containing liquid reaction solution was recycled back to reactor 1.

The hydroformylation experiment was carried out continuously for about 33 days. During the first 15 days of operation the aldehyde product was separated from the liquid reaction solution at about 115°C and 0.15-0.18 MPa (22-26 psia.); from day 16 to day 19 this separation was conducted at about 117°C and 0.15-0.18 MPa (22-26 psia); from day 19 through day 22 this separation was conducted at about 123°C and 0.15-0.18 MPa (22-26 psia.) and from day 23 to day 32.5 this separation was conducted at 133°C and 0.15-0.18 MPa (22-26 psia).

The data set forth in Table 19 below describes the operating conditions and performance in gram moles per liter per hour of 3-methylbutyraldehyde product over about 33 days of continuous hydroformylation.

TABLE 19

Days of Operation	6.9	13.9	21.8	32.5
Reactor No. 1				
Temperature, °C	95.0	95.0	94.9	95.5
Pressure, (psia)kPa	1.27(185)	1.27(185)	1.27(185)	1.27(185)
H_2, (psia)kPa	0.500(72.7)	0.488(70.8)	0.486(70.6)	0.431(62.5)
CO, (psia) kPa	0.399(57.9)	0.380(55.2)	0.366(53.1)	0.385(55.9)
Isobutylene, (psia)kPa	0.236(34.3)	0.258(37.5)	0.274(39.7)	0.323(46.9)
Reactor No. 2				
Temperature, °C	95.3	95.4	95.5	95.4
Pressure, (psia)kPa	1.14(165)	1.14(165)	1.14(165)	1.14(165)
H_2, (psia)kPa	0.526(76.3)	0.517(75.0)	0.503(73.0)	0.455(66.1)
CO, (psia)kPa	0.333(48.4)	0.298(43.3)	0.339(49.2)	0.367(53.6)
Isobutylene, (psia)kPa	0.094(13.7)	0.106(15.4)	0.113(16.4)	0.167(24.3)
Results				
3-Methylbutyraldehyde (g mol/l/hr)	1.77	1.81	1.74	1.49

The rhodium inventory in the reactor system was monitored daily during the course of the experiment and no detectable loss of rhodium in the reactor system was observed over the first 26 days of continuous hydroformylation. However, continued analysis showed that about a 10 percent loss of rhodium inventory in the reactor system occurred over the continuous period from day 26 to day 32.5 (completion of the experiment).

The above experiment demonstrates the high rhodium complex catalyst activity and stability obtained in employing methyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand when hydroformylating even a normally highly unreactive olefin, such as isobutylene. In addition, said experiment demonstrates that the use of a ligand such as methyl [3,3'-di-t-buty1-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite permitted the crude aldehyde product to be separated from the liquid reaction solution at vaporization temperatures even as high as about 120°C without experiencing any loss in rhodium inventory over a prolonged period of operation, while the steady production of 3-methylbutyraldehyde indicates the ligand's high stability against in situ phosphite decomposition to undesirable hydroxy alkyl phosphonic acid by-product.

EXAMPLE 22

Butene-1 was hydroformylated in the same manner as in Example 12 using beta-naphthyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite as the ligand, (Ligand C of Example 17).

The hydroformylation was conducted in a glass reactor operating in a continuous single pass butene-1 hydroformylation mode. The reactor consisted of a 90 ml (three ounce) pressure bottle submersed in an oil bath with a glass front for viewing. About 20 ml of a freshly prepared rhodium catalytic precursor solution was charged to the reactor with a syringe after purging the system with nitrogen. The precursor solution contained about 25 ppm rhodium introduced as rhodium dicarbonyl acetylacetonate, about 2.0 weight

percent ligand (about 155 mole equivalents of beta-naphthyl [3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl] phosphite ligand per mole of rhodium metal) and valeraldehyde trimer as the solvent. After closing the reactor, the system was again purged with nitrogen and the oil bath was heated to furnish the desired hydroformylation reaction temperature. The hydroformylation reaction was conducted at a total gas pressure of about 1.2 MPa (160 psig.), the partial pressures of hydrogen, carbon monoxide, and butene-1 being given in Table 20 below, the remainder being nitrogen and aldehyde product. The flows of the feed gases (carbon monoxide, hydrogen and butene-1) were controlled individually with mass flow meters and the feed gases dispersed into the precursor solution via fritted glass spargers. The unreacted portion of the feed gases stripped out the product C_5 aldehydes and the outlet gas analyzed over about 14 days of continuous operation at the reaction temperature of about 90°C. given in TABLE 20 below. The average reaction rates for each experiment in terms of gram moles per liter per hour of product C_5 aldehydes as well as the linear n-valeraldehyde to 2-methylbutyraldehyde branched product ratio are given in TABLE 20 below. The decreasing reaction rate of C_5 aldehydes produced over time is considered attributable to the very low concentration of rhodium employed.

TABLE 20

TEST RESULTS - DAILY AVERAGES

Days Operm.	Temp. °C.	Partial Pressures			Reaction Rate gram moles/ Liter/Hour	Linear/Branched Aldehyde Mole Ratio
		CO H_2 (psia)	H_2 (psia)	Butene-1 H_2 (psia)		
0.5	90	0.08 (12)	0.30 (44)	0.26 (38)	1.1	4.0
1.5	90	0.06 (9)	0.28 (40)	0.24 (35)	1.5	4.0
2.5	90	0.06 (8)	0.24 (38)	0.21 (30)	1.7	3.7
3.5	90	0.06 (9)	0.28 (41)	0.17 (25)	1.5	4.0
4.5	90	0.07 (10)	0.29 (42)	0.19 (28)	1.2	4.0
5.5	90	0.08 (11)	0.29 (42)	0.20 (29)	1.0	5.0
7.5	90	0.08 (12)	0.30 (43)	0.21 (30)	0.7	6.0
8.5	90	0.08 (12)	0.30 (43)	0.14 (20)	0.5	7.0
9.5	90	0.08 (12)	0.30 (44)	0.19 (27)	0.5	8.0
10.5	90	0.08 (12)	0.30 (43)	0.19 (28)	0.5	9.0
11.5	90	0.08 (12)	0.30 (43)	0.19 (28)	0.6	9.0
12.5	90	0.08 (12)	0.30 (44)	0.19 (28)	0.5	8.0
13.5	90	0.08 (12)	0.30 (44)	0.19 (28)	0.5	8.0
13.9	90	0.08 (12)	0.30 (43)	0.20 (29)	0.4	8.0

EXAMPLE 23

A similar continuous hydroformylation experiment as set forth in Example 10 was conducted and the formation of hydroxyalkyl phosphonic acid monitored.

The hydroformylation reaction was conducted by charging about 770 mL of a catalyst precursor solution of rhodium dicarbonyl acetylacetonate (about 492 ppm rhodium), about 3.5 wt. % 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4 -methylphenyl) phosphite ligand (about 16.8 mole equivalents of ligand per mole of rhodium), and about 96.3 wt. % of C_5 aldehyde (about 69.3 wt % valeraldehyde and about 27 wt % valeraldehyde trimer) as solvent to reactor 1. About 900 milliliters of the same catalyst precursor solution

was charged to reactor 2. The start-up and operating procedures set forth in Example 10 were employed.

The hydroformylation reaction conditions as well as the rate of C_5 aldehydes produced in terms of gram moles per liter per hour and the linear to branched aldehyde product ratio of n-valeraldehyde to 2-methybutyraldehyde are given in TABLE 21 below.

TABLE 21

Days of Operation	7	11	12
Butene Feed, mol %			
Butene-1	41.9	37.4	40.2
Trans-Butene-2	35.1	38.2	36.4
Cis-Butene-2	22.9	24.4	23.4
Reactor No. 1			
Temperature, °C	70.4	65.6	65.1
Pressure, (psia) MPa	0.14 (205)	0.14 (205)	0.14 (205)
H_2, (psia) MPa	0.611 (88.7)	0.595 (86.4)	0.568 (82.4)
CO, (psia) MPa	0.136 (19.7)	0.227 (33.0)	0.323 (46.9)
Butene-1, (psia) MPa	0.027 (3.9)	0.039 (5.6)	0.067 (9.7)
Trans-Butene 2 and Cis-Butene-2, (psia) MPa	0.268 (38.9)	0.274 (39.7)	0.271 (39.4)
Reactor No. 2			
Temperature, °C	90.7	95.5	95.3
Pressure, (psia) MPa	1.27 (185)	1.27 (185)	1.27 (185)
H_2, (psia) MPa	0.614 (89.1)	0.537 (77.9)	0.480 (69.7)
CO, (psia) MPa	0.059 (8.6)	0.160 (23.2)	0.274 (39.7)
Butene-1, (psia) MPa	0.010 (1.4)	0.016 (2.3)	0.015 (2.2)
Trans-Butene-2 and Cis-Butene-2, (psia) MPa	0.256 (37.1)	0.318 (46.1)	0.342 / (49.7)
Results			
C_5 Aldehydes, gmol/l/hr	2.89	2.76	2.31
Linear/Branched Aldehyde Ratio	1.87	1.34	1.39

During this hydroformylation experiment the hydroformylation reaction medium was monitored by routinely withdrawing samples of the continuous catalyst-containing hydroformylation reaction medium from reactor 1 and examining same via ^{31}P NMR spectroscopy for a detectable signal (resonance peak) of alpha-hydroxypentyl phosphonic acid. A comparative synthetic solution containing 100 ppm (concentration by weight) of alpha-hydroxypentyl phosphonic acid which gave a detectable phosphonic acid signal (resonance peak) at about 25.8 ppm relative to external H_3PO_4 in the ^{31}P NMR after 2000 pulses (transients) was employed as the standard. Such set the low detection limit of the alpha-hydroxypentyl phosphonic acid at about 100 ppm (concentration by weight).

After about 10 days of continuous hydroformylation no detectable amount of alpha-hydroxypentyl phosphonic acid showed up on the ^{31}P NMR spectrum. At day 11 of the continuous operation however, a

small qualitative amount of alpha-hydroxypentyl phosphonic acid had formed as evidenced by a small phosphonic acid resonance peak that appeared on the spectrum of the ^{31}P NMR conducted that day. At this point on day 11 an Amberlyst® A-21 ion exchange resin bed was employed in the catalyst recycle line of the liquid recycle process and the catalyst containing recycle solution, after removal of the desired aldehyde product, passed through said bed on its return to the reactor. Within hours the alpha-hydroxypentyl phosphonic acid was scavenged from the hydroformylation reaction medium as evidenced by the disappearance of the detectable phosphonic acid peak in the ^{31}P NMR spectrum for the sample of the hydroformylation reaction medium recorded on day 12. Note in this experiment a commercial grade Amberlyst® A-21 resin was employed. Apparently this resin contained chloride impurities which contaminated (poisoned) a portion of the rhodium catalyst, as evidenced by new rhodium-ligand complex peaks on the ^{31}P NMR spectra.

EXAMPLE 24

A similar continuous hydroformylation experiment as set forth in Example 10 was conducted and the formation of hydroxyalkyl phosphonic acid monitored.

The hydroformylation reaction was conducted by charging about 770 mℓ of a catalyst precursor solution of rhodium dicarbonyl acetylacetonate (about 300 ppm rhodium), about 2.0 wt. % 1,1'-biphenyl-2,2'-diyl-(2,6-di-tert-butyl-4 -methylphenyl) phosphite ligand (about 15.8 mole equivalents of ligand per mole of rhodium)and about 98 wt. % of C_5 aldehyde (about 70 wt % valeraldehyde and about 28 wt % valeraldehyde trimer) as solvent to reactor 1. About 900 milliliters of the same catalyst precursor solution was charged to reactor 2. The start-up and operating procedures set forth in Example 10 were employed. In this experiment a purified Amberlyst® A-21 ion exchange resin bed was employed from the start of the process. Said bed was situated in the catalyst recycle line so that the recycled rhodium catalyst containing liquid reaction medium after removal of the desired aldehyde product passed through said bed on its return to the reactor. On day 1 of the process an additional amount of the same phosphite ligand was added to make up for the low concentration in the original charge. On day 7 the Amberlyst resin bed was replaced with a new purified Amberlyst® A-21 ion exchange resin bed. On day 8 the system was shut down for two hours due to a power failure. On day 14 the rhodium complex catalysts were removed from both reactors because reactor liquid level control indications appeared erroneous. On day 15 fresh rhodium dicarbonyl acetylacetonate was added to raise the reaction rate and an additional amount of the same phosphite ligand employed was added to maintain target concentration.

The hydroformylation reaction conditions as well as the rate of C_5 aldehydes produced in terms of gram moles per liter per hour and the linear to branched aldehyde product ratio of n-valeraldehyde to 2-methylbutyraldehyde are given in TABLE 22 below.

TABLE 22

Days of Operation	7	16	22
Butene Feed, mol %			
Butene-1	42.6	46.1	43.5
Trans-Butene-2	34.6	30.5	32.5
Cis-Butene-2	22.8	23.3	24.0
Reactor No. 1			
Temperature, °C	85	85.5	85.4
Pressure, (psia) MPa	1.41 (205)	1.41 (205)	1.41 (205)
H_2, (psia) MPa	0.595 (86.4)	0.641 (93.1)	0.600 (87.1)
CO, (psia) MPa	0.185 (27.5)	0.056 (8.1)	0.088 (12.7)
Butene-1, (psia) MPa	0.047 (6.8)	0.044 (6.4)	0.050 (7.3)
Trans-Butene 2 and Cis-Butene-2, (psia) MPa	0.362 (52.6)	0.391 (56.8)	0.422 (61.2)
Reactor No. 2			
Temperature, °C	95.2	95.3	96.7
Pressure, (psia) MPa	1.27 (185)	1.27 (185)	1.27 (185)
H_2, (psia) MPa	0.539 (78.2)	0.487 (70.7)	0.476 (69.0)
CO, (psia) MPa	0.104 (15.1)	0.103 (15.0)	0.110 (16.0)
Butene-1, (psia) MPa	0.019 (2.7)	0.025 (3.6)	0.026 (3.8)
Trans-Butene-2 and Cis-Butene-2, (psia) MPa	0.365 (53.0)	0.459 (66.6)	0.483 (70.1)
Results			
C_5 Aldehydes, gmol/l/hr	3.31	3.15	3.01
Linear/Branched Aldehyde Ratio	1.59	1.91	1.81

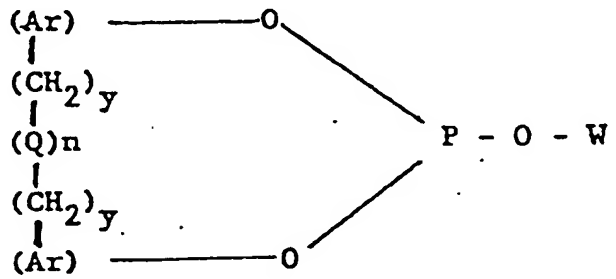
During this hydroformylation experiment the hydroformylation reaction medium was monitored for alpha-hydroxypentyl phosphonic acid via the same ^{31}P NMR procedure of Example 23. ^{31}P NMR spectra of samples of the hydroformylation reaction medium taken from reactor 1 on days 7, 16 and 22 of the continuous process showed no detectable amounts of alpha-hydroxypentyl phosphonic acid decomposition product. Moreover, in this experiment the commercial grade Amberlyst® A-21 ion exchange resin bed was purified before use via a series of elution washings to remove contaminate chlorides and aluminum oxy polymers (oligomers). The purification of the resin was conducted as follows. A 250 gram (630 ml) portion of the resin was charged to a 50 cm x 36 mm glass column equipped with a stopcock and containing a glass wool plug. The resin was washed with the following solvents at the given rate of bed volumes per hour: (a) three bed volumes (1890 ml) of 10% aqueous HCl; (b) four bed volumes (2520 ml) of 5% aqueous NaOH; (c) five bed volumes (3150 ml) of deionized water; (d) four bed volumes (2520 ml) of methanol and (e) three bed volumes (1890 ml) of toluene. The resin was then discharged from the column to a one-liter flask and dried at about 40 °C and 1.3 kPa (10 mm Hg) pressure using a rotary evaporator. It is noteworthy that no chloride-rhodium complexes showed up on the ^{31}P NMR spectra of this experiment which employed the purified Amberlyst® A-21 resin.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL, SE

1. A hydroformylation process for producing aldehydes which comprises reacting an olefinically unsaturated organic compound with carbon monoxide and hydrogen in the presence of a rhodium complex

catalyst consisting essentially of rhodium complexed with carbon monoxide and a diorganophosphite ligand, and in the added presence of a free diorganophosphite ligand, characterized in that the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand are each individually ligands having the formula



(I)

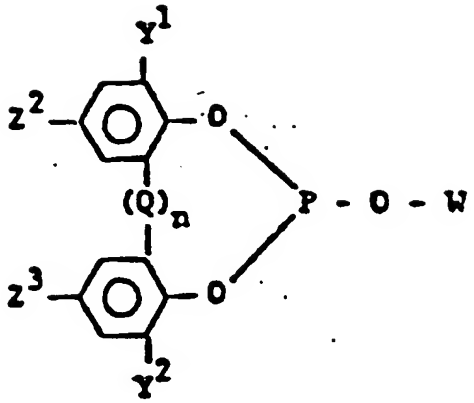
wherein each y individually has a value of 0 or 1; n has a value of 0 or 1; Q is a divalent bridging group selected from $-CH_2-$, $-CH(CH_3)-$ and -S-;
W is an unsubstituted or substituted C_1-C_{18} alkyl or an unsubstituted or substituted C_6-C_{18} aryl group; and each Ar represents an identical or different unsubstituted or substituted aryl group selected from phenylene, naphthylene and anthracylene;
said substituent(s) on W and Ar being selected from C_1-C_{18} alkyl groups , phenyl, naphthyl, benzyl, phenylethyl, tolyl, xylyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, halogen, nitro, cyano, trifluoromethyl, hydroxy, $-Si(R^6)_3$, $-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$, $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$ wherein R^6 individually represents the same or different hydrocarbon groups selected from C_1-C_{18} alkyl groups and aryl, aralkyl, alkaryl and alicyclic groups containing from 6 to 18 carbon atoms with the proviso that in substituents $-N(R^6)_2$ each R^6 taken together can also represent a divalent bridging group that forms a heterocyclic group with the nitrogen atom and in substituents $-N(R^6)_2$,$-C(O)N(R^6)_2$ and $-N(R^6)C(O)R^6$ each R^6 bonded to N can also be hydrogen while in substituents $-P(O)(R^6)_2$ one R^6 can also be hydrogen; said Ar groups being bonded through the ortho positions in relation to the oxygen atoms that connect the Ar groups to the phosphorus atom; and any substituent, when present on such Ar groups or an aryl group W, being bonded in the para and/or ortho position of the aryl group in relation to the oxygen atom that bonds the given substituted aryl group to the phosphorus atom,
provided that in case W is an aryl group at least one of said aryl groups Ar and W is substituted and not all of the total accumulative number of ortho positions on Ar and W are substituted with a radical having a steric hindrance of isopropyl or greater.

2. A process as defined in claim 1, wherein the olefinically unsaturated compound is selected from alpha-olefins containing from 2 to 20 carbon atoms, internal olefins containing from 4 to 20 carbon atoms, and mixtures of such alpha and internal olefins.

3. A process as defined in claim 2 wherein the olefin starting material is selected from butene-1, butene-2, isobutylene, and an olefin mixture consisting essentially of butene-1 and butene-2.

4. A process as defined in any one of claims 1 to 3 wherein the hydroformylation reaction conditions comprise a reaction temperature in the range of from 50°C to 120°C, a total gas pressure of hydrogen, carbon monoxide and olefinically unsaturated organic compound of from 6.9 to 10340 kPa (1 to 1500 psia), a hydrogen partial pressure of from 100 to 1100 kPa (15 to 160 psia), a carbon monoxide partial pressure of from 6.9 to 828 kPa (1 to 120 psia), and wherein the reaction medium contains from 4 to 50 moles of said diorganophosphite ligand per mole of rhodium in said medium.

5. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having the formula



(II)

wherein Q is $-CH_2-$ or $-CHCH_3-$; n is 0 or 1; Y^1, Y^2, Z^2 and Z^3 are hydrogen or the same as the substituents on Ar and W defined in claim 1 with the proviso that both Y^1 and Y^2 are groups having a steric hindrance of isopropyl or greater; and W represents an unsubstituted C_1-C_{18} alkyl group.

6. A process as defined in claim 5 wherein Y^1 and Y^2 are branched alkyl groups having from 3 to 5 carbon atoms and wherein W is an unsubstituted C_1-C_{10} alkyl group.

7. A process as defined in claim 6 wherein Y^1 and Y^2 are t-butyl groups, Q is $-CH_2-$ and W is an unsubstituted C_1-C_8 alkyl group.

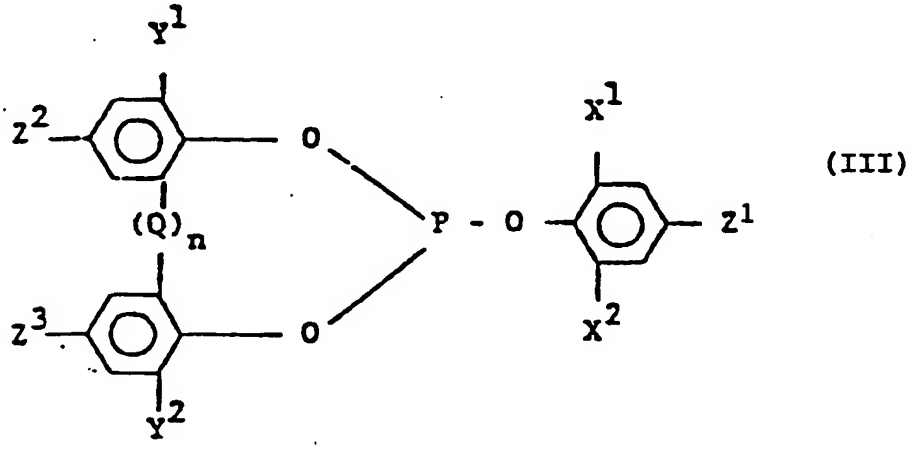
8. A process as defined in any one of claims 1 to 4 wherein W is a phosphonyl substituted alkyl group of the formula

$$-[C(R^7)_2]_pP(O)(R^6)_2$$

wherein each R^6 is the same or different and is individually selected from C_1-C_{18} alkyl, phenyl and cyclohexyl; each R^7 is the same or different and is individually selected from hydrogen and C_1-C_4 alkyl; p is an integer of from 1 to 10; with the proviso that one R^6 can also be hydrogen.

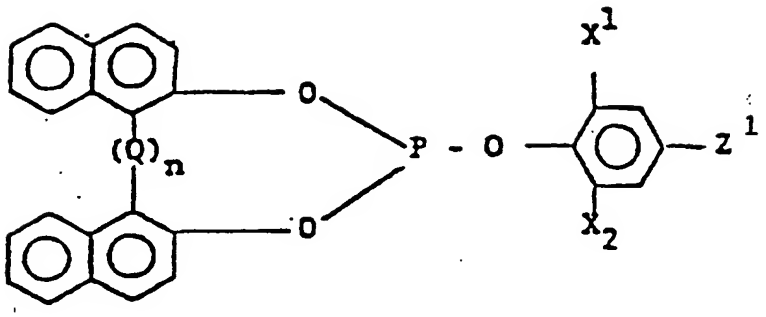
9. A process as defined in claim 8 wherein W is a $-CH_2CH_2P(O)(C_6H_5)_2$ group.

10. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having a formula selected from



(III)

and

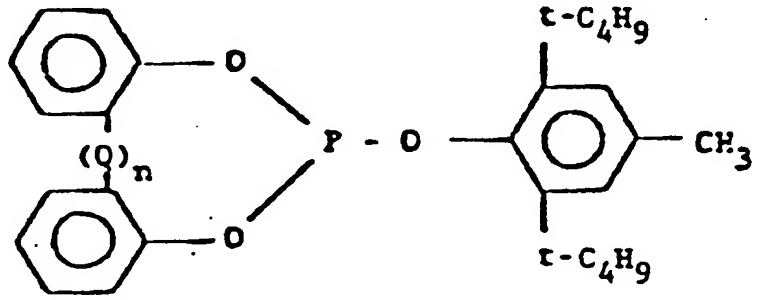


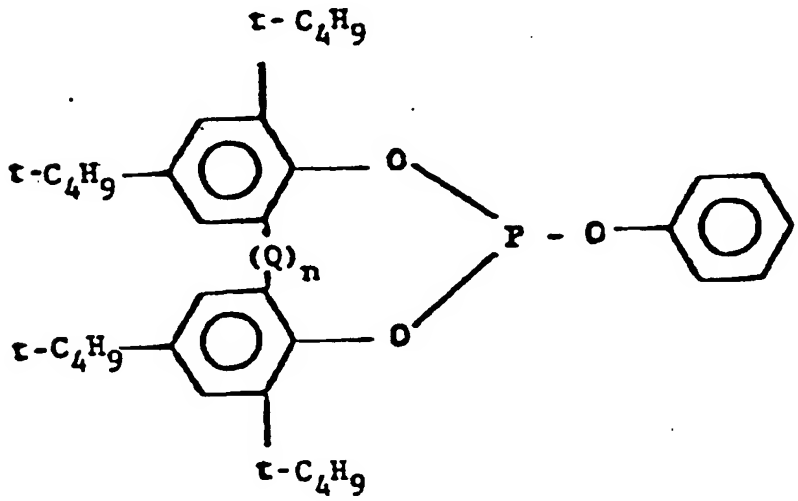
(IV)

wherein n has a value of 0 or 1; Q is $-CH_2-$ or $-CHCH_3-$; Y^1, Y^2, X^1, X^2, Z^1, Z^2 and Z^3 are hydrogen or have the meanings given in claim 1 for the substituents on W and Ar, with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite of formulae (III) and (IV) are groups having a steric hindrance of isopropyl or greater, and with the proviso that in formula (III) no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

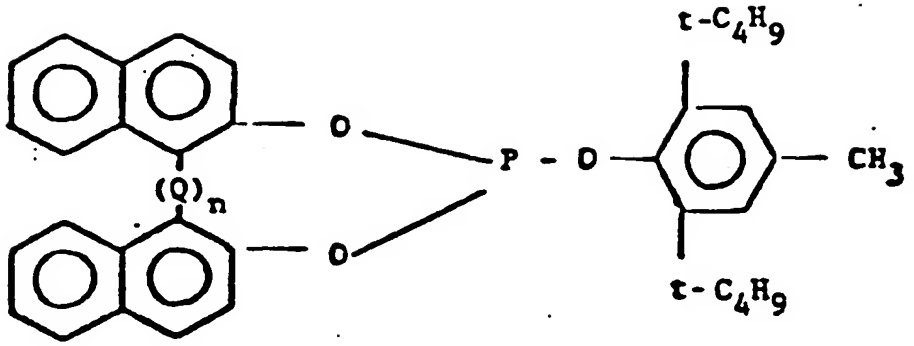
11. A process as defined in claim 10 wherein Y^1 and Y^2 are branched chain alkyl groups having from 3 to 5 carbon atoms.

12. A process as defined in claim 10 wherein the diorganophosphite ligand is selected from

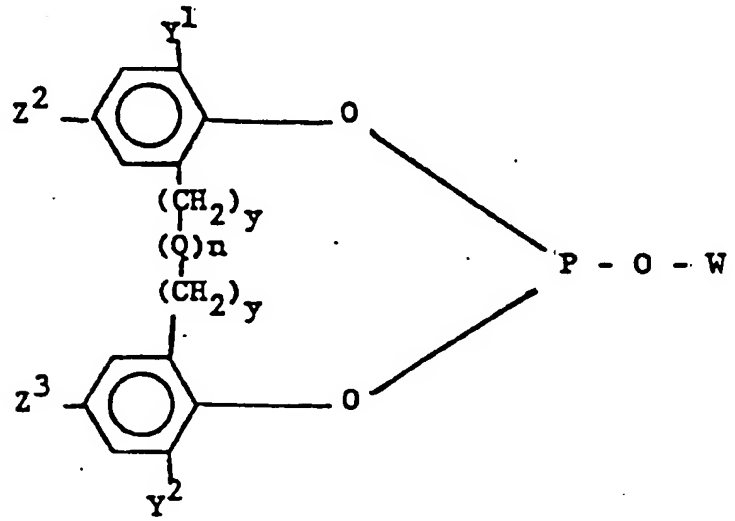




and



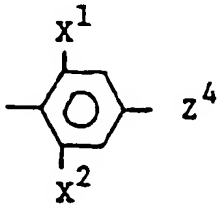
13. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having the formula



(V)

wherein Z^2 and Z^3 each individually represent a group selected from hydroxy and $-OR^6$; y, n, R^6, Q and W are the same as defined in claim 1, and Y^1, Y^2 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W.

14. A process as defined in claim 13 wherein each y has a value of zero; Q is $-CH_2-$ or $-CHCH_3-$; R^6 is a C_1-C_{10} alkyl group; Y^1 and Y^2 each individually are selected from hydrogen, branched chain C_3-C_{12} alkyl groups, phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl; and W is selected from C_1-C_{18} alkyl groups, alpha-naphthyl, beta-naphthyl and an aryl group of the formula



wherein X^1, X^2 and Z^4 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite ligand are groups having a steric hindrance of isopropyl or greater, and with

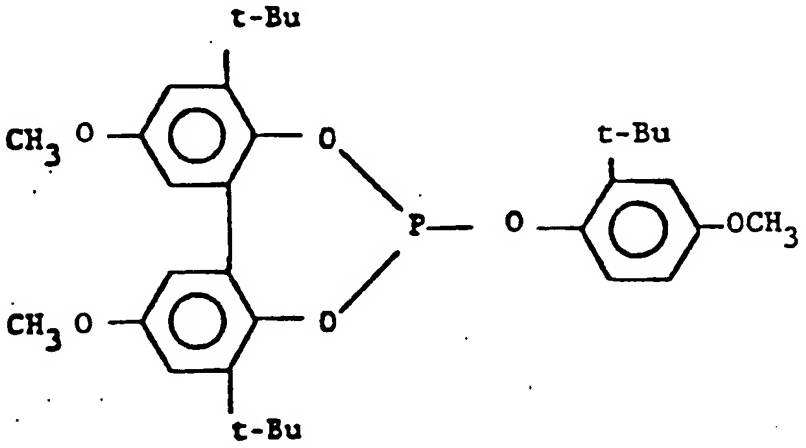
the proviso that no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

15. A process as defined in claim 14 wherein Z^2 and Z^3 each represent $-OR^6$, R^6 representing C_1-C_{10} alkyl; Y^1 and Y^2 are both branched chain C_3-C_5 alkyl groups; and W is a C_1-C_{10} alkyl group.

16. A process as defined in claim 15 wherein Z^2 and Z^3 each represent methoxy; Y^1 and Y^2 each represent tertiary butyl; and W represents methyl.

17. A process as defined in claim 15 wherein n is zero.

18. A process as defined in claim 13 wherein the diorganophosphite complexed with the rhodium and the free diorganophosphite ligand also present is



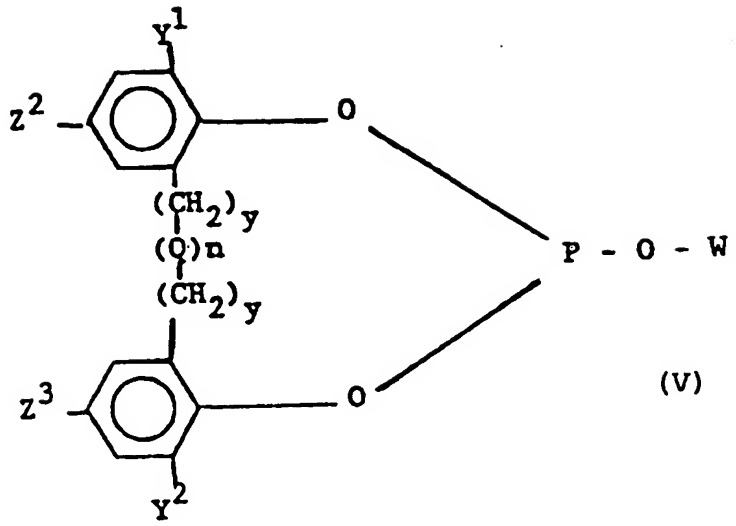
19. A process as defined in any one of claims 1 to 18, which comprises minimizing decomposition of the free diorganophosphite ligand by
    (a) removing a portion of the liquid hydroformylation reaction medium from the hydroformylation reaction zone,
    (b) treating the liquid medium so removed with a weakly basic anion exchange resin, and
    (c) returning the treated reaction medium to the hydroformylation reaction zone.

20. A process as defined in any one of claims 1 to 19 wherein the hydroformylation comprises a continuous catalyst containing liquid recycle procedure.

21. A process as defined in claim 20 which comprises removing a portion of liquid hydroformylation reaction medium from the hydroformylation reaction zone and passing said medium, either prior to and/or after separation of aldehyde product therefrom, through a weakly basic anion exchange resin bed.

22. A process as defined in any one of claims 19 to 21 wherein said weakly basic anion exchange resin comprises a crosslinked tertiary amine polystyrene anion exchange resin of the gel or macroreticular type.

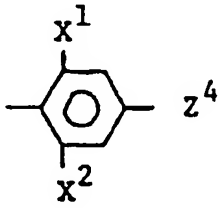
23. A diorganophosphite ligand having the general formula



(V)

wherein Z^2 and Z^3 each individually represent a group selected from hydroxy and $-OR^6$; y, n, R^6, Q and W are the same as defined in claim 1, and Y^1, Y^2 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W, provided that in case W is a substituted aryl group, said substituent(s) is(are) bonded to the para and/or ortho position of the aryl group in relation to the oxygen atom that bonds said aryl group to the phosphorus atom and also provided that at least one of Y^1, Y^2, Z^2, Z^3 and the substituents on an aryl group W, if any, is different from hydrogen and not all of the total available ortho positions on the aryl groups present have a steric hindrance of isopropyl or greater.

24. A diorganophosphite ligand as defined in claim 23 wherein each Y has a value of zero; Q is $-CH_2-$ or $-CHCH_3-$; R^6 is a C_1-C_{10} alkyl group; Y^1 and Y^2 each individually are selected from hydrogen, branched chain C_3-C_{12} alkyl groups, phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl; and W is selected from C_1-C_{18} alkyl groups, alpha-naphthyl, beta-naphthyl and an aryl group of the formula



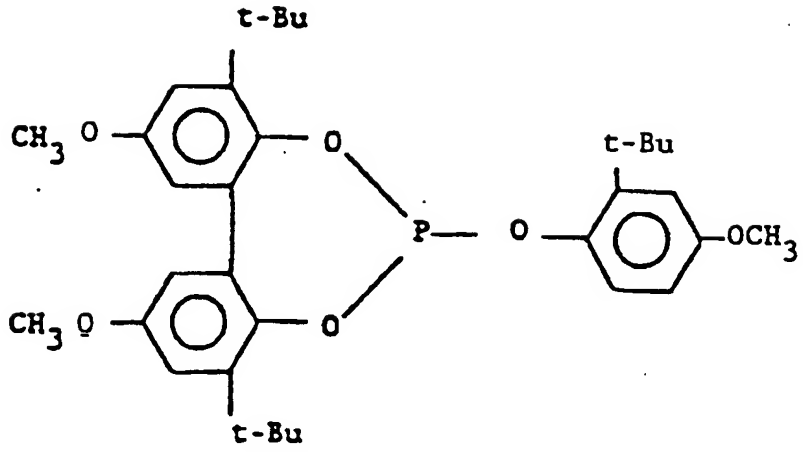
wherein X^1, X^2 and Z^4 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite ligand are groups having a steric hindrance of isopropyl or greater, and with the proviso that no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

25. A ligand as defined in claim 24 wherein Z^2 and Z^3 each represent $-OR^6$, R^6 representing C_1-C_{10} alkyl; Y^1 and Y^2 are both branched chain C_3-C_5 alkyl groups; and W is a C_1-C_{10} alkyl group.

26. A ligand as defined in claim 25 wherein Z^2 and Z^3 each represent methoxy; Y^1 and Y^2 each represent tertiary butyl; and W represents methyl.

27. A ligand as defined in claim 26 wherein n is zero.

28. A ligand as defined in claim 23 having the formula:



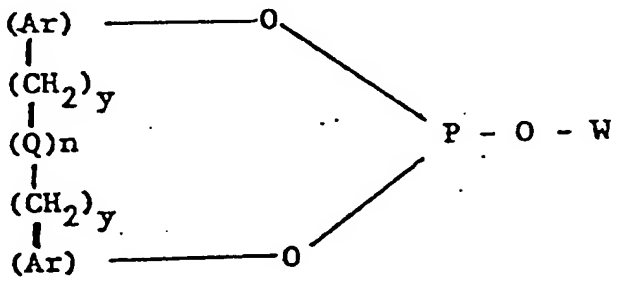
29. A rhodium complex hydroformylation catalyst comprising rhodium complexed with a diorganophosphite ligand as defined in any one of claims 23 to 28.

30. A rhodium complex hydroformylation catalytic precursor composition consisting essentially of solubilized rhodium diorganophosphite complex, an organic solvent, and free diorganophosphite ligand, characterized in that the diorganophosphite ligand of said complex and free diorganophosphite ligand is a ligand as defined in claim 1.

31. A composition as defined in claim 30 wherein the rhodium-diorganophosphite complex is a rhodium carbonyl diorganophosphite acetylacetonate complex.

Claims for the following Contracting State : AT

1. A hydroformylation process for producing aldehydes which comprises reacting an olefinically unsaturated organic compound with carbon monoxide and hydrogen in the presence of a rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and a diorganophosphite ligand, and in the added presence of a free diorganophosphite ligand, characterized in that the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand are each individually ligands having the formula



(I)

wherein each y individually has a value of 0 or 1; n has a value of 0 or 1; Q is a divalent bridging group selected from $-CH_2-$, $-CH(CH_3)-$ and -S-;
W is an unsubstituted or substituted C_1-C_{18} alkyl or an unsubstituted or substituted C_6-C_{18} aryl group; and each Ar represents an identical or different unsubstituted or substituted aryl group selected from phenylene, naphthylene and anthracylene;
said substituent(s) on W and Ar being selected from C_1-C_{18} alkyl groups , phenyl, naphthyl, benzyl, phenylethyl, tolyl, xylyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, halogen, nitro, cyano, trifluoromethyl, hydroxy, $-Si(R^6)_3$, $-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$, $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$ wherein R^6 individually repre-

sents the same or different hydrocarbon groups selected from C_1-C_{18} alkyl groups and aryl, aralkyl, alkaryl and alicyclic groups containing from 6 to 18 carbon atoms with the proviso that in substituents $-N(R^6)_2$ each R^6 taken together can also represent a divalent bridging group that forms a heterocyclic group with the nitrogen atom and in substituents $-N(R^6)_2$,$-C(O)N(R^6)_2$ and $-N(R^6)C(O)R^6$ each R^6 bonded to N can also be hydrogen while in substituents $-P(O)(R^6)_2$ one R^6 can also be hydrogen; said Ar groups being bonded through the ortho positions in relation to the oxygen atoms that connect the Ar groups to the phosphorus atom; and any substituent, when present on such Ar groups or an aryl group W, being bonded in the para and/or ortho position of the aryl group in relation to the oxygen atom that bonds the given substituted aryl group to the phosphorus atom,

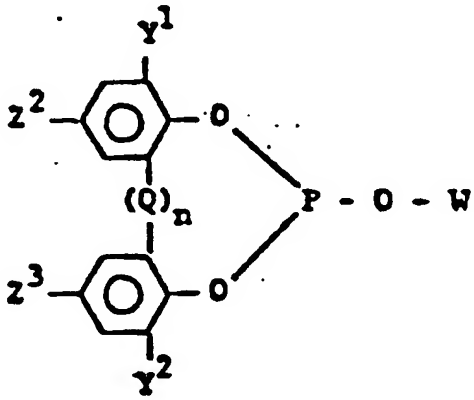
provided that in case W is an aryl group at least one of said aryl groups Ar and W is substituted and not all of the total accumulative number of ortho positions on Ar and W are substituted with a radical having a steric hindrance of isopropyl or greater.

2. A process as defined in claim 1, wherein the olefinically unsaturated compound is selected from alpha-olefins containing from 2 to 20 carbon atoms, internal olefins containing from 4 to 20 carbon atoms, and mixtures of such alpha and internal olefins.

3. A process as defined in claim 2 wherein the olefin starting material is selected from butene-1, butene-2, isobutylene, and an olefin mixture consisting essentially of butene-1 and butene-2.

4. A process as defined in any one of claims 1 to 3 wherein the hydroformylation reaction conditions comprise a reaction temperature in the range of from 50°C to 120°C, a total gas pressure of hydrogen, carbon monoxide and olefinically unsaturated organic compound of from 6.9 to 10340 kPa (1 to 1500 psia), a hydrogen partial pressure of from 100 to 1100 kPa (15 to 160 psia), a carbon monoxide partial pressure of from 6.9 to 828 kPa (1 to 120 psia), and wherein the reaction medium contains from 4 to 50 moles of said diorganophosphite ligand per mole of rhodium in said medium.

5. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having the formula



(II)

wherein Q is $-CH_2-$ or $-CHCH_3-$; n is 0 or 1; Y^1, Y^2, Z^2 and Z^3 are hydrogen or the same as the substituents on Ar and W defined in claim 1 with the proviso that both Y^1 and Y^2 are groups having a steric hindrance of isopropyl or greater; and W represents an unsubstituted C_1-C_{18} alkyl group.

6. A process as defined in claim 5 wherein Y^1 and Y^2 are branched alkyl groups having from 3 to 5 carbon atoms and wherein W is an unsubstituted C_1-C_{10} alkyl group.

7. A process as defined in claim 6 wherein Y^1 and Y^2 are t-butyl groups, Q is $-CH_2-$ and W is an unsubstituted C_1-C_8 alkyl group.

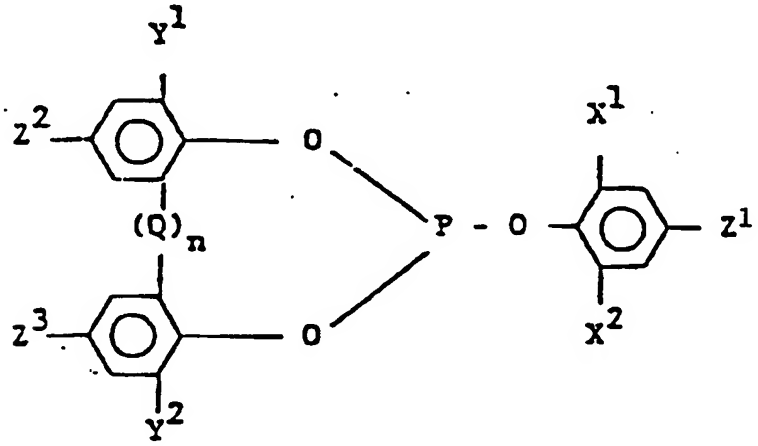
8. A process as defined in any one of claims 1 to 4 wherein W is a phosphonyl substituted alkyl group of the formula

$-[C(R^7)_2]_pP(O)(R^6)_2$

wherein each R^6 is the same or different and is individually selected from C_1-C_{18} alkyl, phenyl and cyclohexyl; each R^7 is the same or different and is individually selected from hydrogen and C_1-C_4 alkyl; p is an integer of from 1 to 10; with the proviso that one R^6 can also be hydrogen.

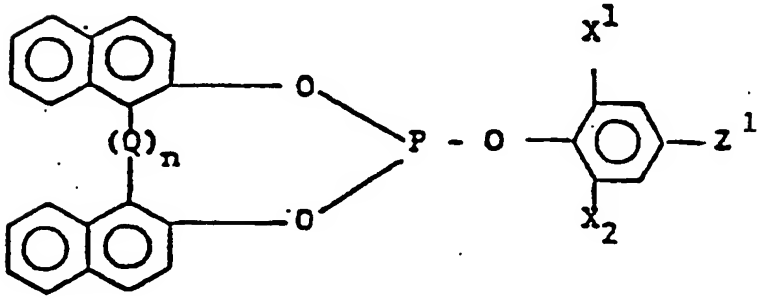
9. A process as defined in claim 8 wherein W is a $-CH_2CH_2P(O)(C_6H_5)_2$ group.

10. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite ligand complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having a formula selected from



(III)

and

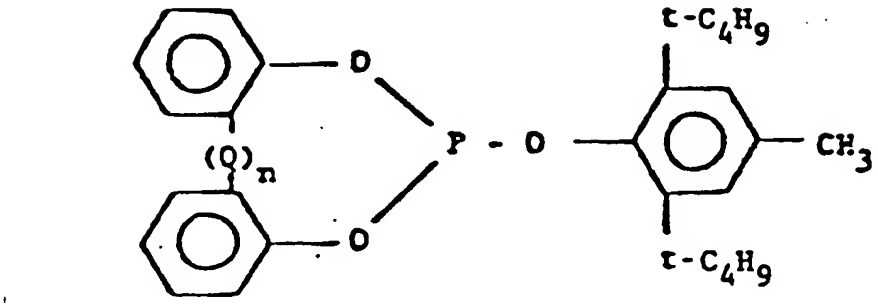


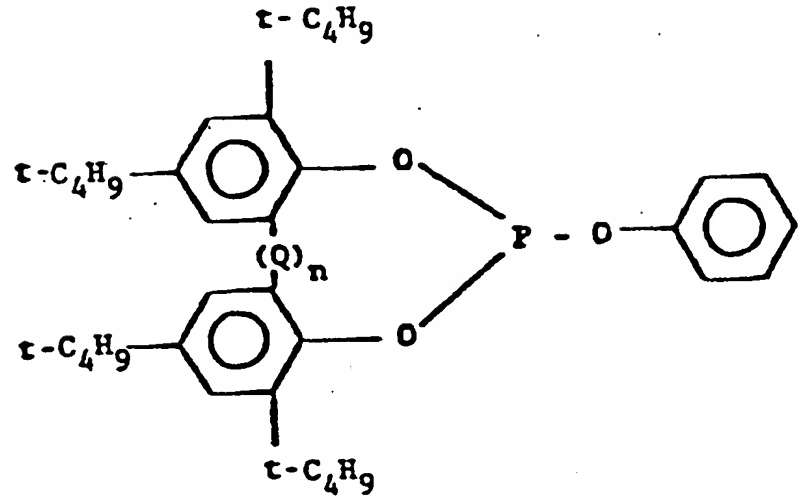
(IV)

wherein n has a value of 0 or 1; Q is $-CH_2-$ or $-CHCH_3-$; Y^1, Y^2, X^1, X^2, Z^1, Z^2 and Z^3 are hydrogen or have the meanings given in claim 1 for the substituents on W and Ar, with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite of formulae (III) and (IV) are groups having a steric hindrance of isopropyl or greater, and with the proviso that in formula (III) no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

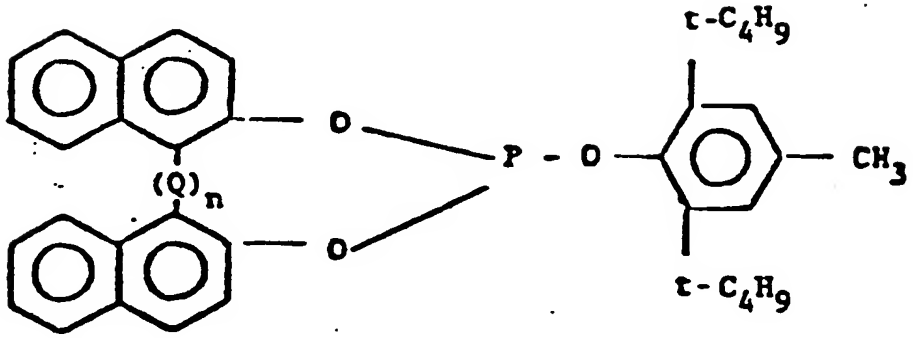
11. A process as defined in claim 10 wherein Y^1 and Y^2 are branched chain alkyl groups having from 3 to 5 carbon atoms.

12. A process as defined in claim 10 wherein the diorganophosphite ligand is selected from

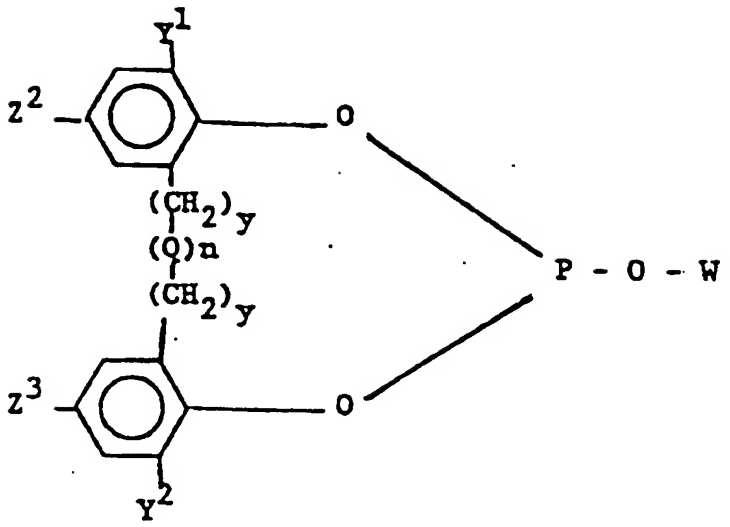




and



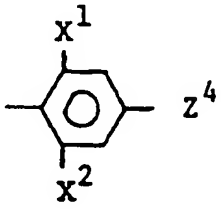
13. A process as defined in any one of claims 1 to 4 wherein the diorganophosphite complexed with the rhodium and the free diorganophosphite ligand also present are each individually ligands having the formula



(V)

wherein Z^2 and Z^3 each individually represent a group selected from hydroxy and $-OR^6$; y, n, R^6, Q and W are the same as defined in claim 1, and Y^1, Y^2 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W.

14. A process as defined in claim 13 wherein each y has a value of zero; Q is $-CH_2-$ or $-CHCH_3-$; R^6 is a C_1-C_{10} alkyl group; Y^1 and Y^2 each individually are selected from hydrogen, branched chain C_3-C_{12} alkyl groups, phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl; and W is selected from C_1-C_{18} alkyl groups, alpha-naphthyl, beta-naphthyl and an aryl group of the formula



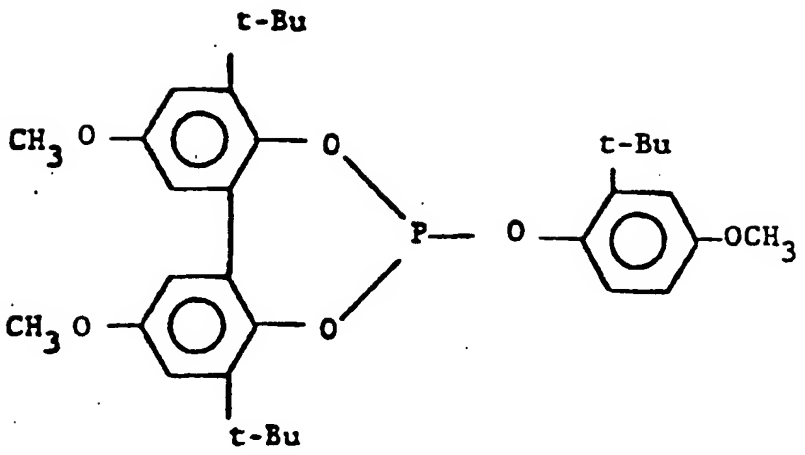
wherein X^1, X^2 and Z^4 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite ligand are groups having a steric hindrance of isopropyl or greater, and with the proviso that no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

15. A process as defined in claim 14 wherein Z^2 and Z^3 each represent $-OR^6$, R^6 representing C_1-C_{10} alkyl; Y^1 and Y^2 are both branched chain C_3-C_5 alkyl groups; and W is a C_1-C_{10} alkyl group.

16. A process as defined in claim 15 wherein Z^2 and Z^3 each represent methoxy; Y^1 and Y^2 each represent tertiary butyl; and W represents methyl.

17. A process as defined in claim 15 wherein n is zero.

18. A process as defined in claim 13 wherein the diorganophosphite complexed with the rhodium and the free diorganophosphite ligand also present is



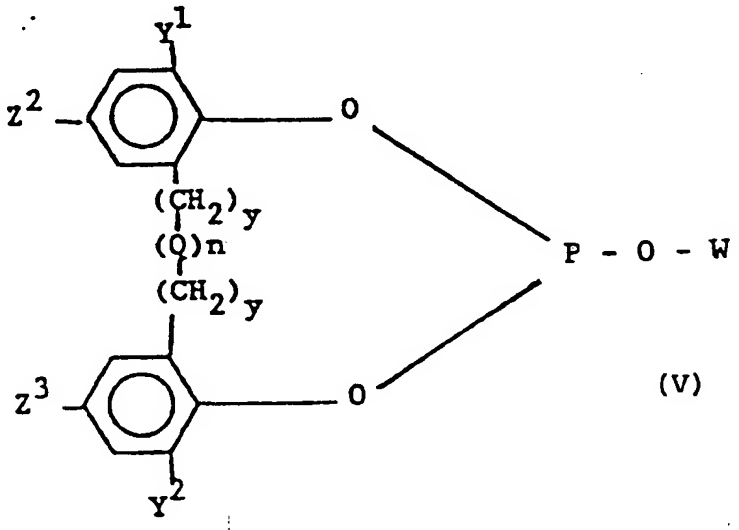
19. A process as defined in any one of claims 1 to 18, which comprises minimizing decomposition of the free diorganophosphite ligand by
    (a) removing a portion of the liquid hydroformylation reaction medium from the hydroformylation reaction zone,
    (b) treating the liquid medium so removed with a weakly basic anion exchange resin, and
    (c) returning the treated reaction medium to the hydroformylation reaction zone.

20. A process as defined in any one of claims 1 to 19 wherein the hydroformylation comprises a continuous catalyst containing liquid recycle procedure.

21. A process as defined in claim 20 which comprises removing a portion of liquid hydroformylation reaction medium from the hydroformylation reaction zone and passing said medium, either prior to and/or after separation of aldehyde product therefrom, through a weakly basic anion exchange resin bed.

22. A process as defined in any one of claims 19 to 21 wherein said weakly basic anion exchange resin comprises a crosslinked tertiary amine polystyrene anion exchange resin of the gel or macroreticular type.

23. A process for preparing a diorganophosphite ligand having the general formula

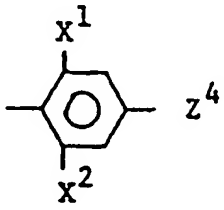


(V)

wherein Z^2 and Z^3 each individually represent a group selected from hydroxy and $-OR^6$; y, n, R^6, Q and

W are the same as defined in claim 1, and Y^1, Y^2 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W, provided that in case W is a substituted aryl group, said substituent(s) is(are) bonded to the para and/or ortho position of the aryl group in relation to the oxygen atom that bonds said aryl group to the phosphorus atom and also provided that at least one of Y^1, Y^2, Z^2, Z^3 and the substituents on an aryl group W, if any, is different from hydrogen and not all of the total available ortho positions on the aryl groups present have a steric hindrance of isopropyl or greater,
which process comprises reacting a corresponding organic diphenolic compound with phosphorus trichloride to form an organic phosphorochloridite intermediate which in turn is reacted with a corresponding mono-hydroxy compound in the presence of an HCl acceptor to produce the desired diorganophosphite ligand.

24. A process as defined in claim 23 wherein each Y has a value of zero; Q is $-CH_2-$ or $-CHCH_3-$; R^6 is a C_1-C_{10} alkyl group; Y^1 and Y^2 each individually are selected from hydrogen, branched chain C_3-C_{12} alkyl groups, phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl; and W is selected from C_1-C_{18} alkyl groups, alpha-naphthyl, beta-naphthyl and an aryl group of the formula



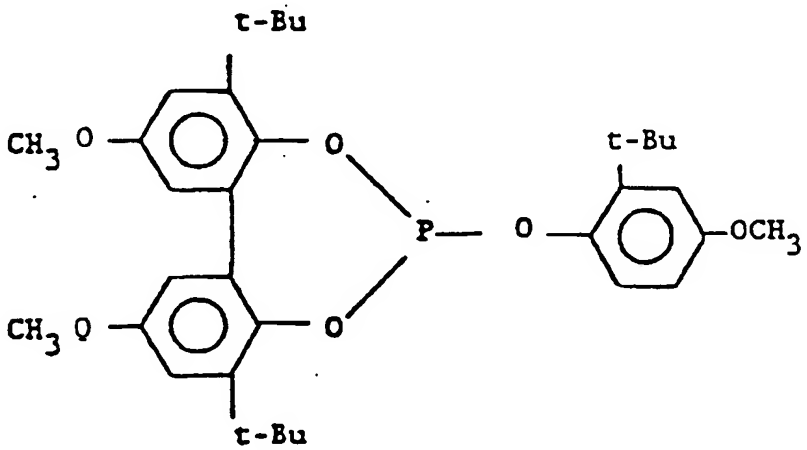
wherein X^1, X^2 and Z^4 are hydrogen or any of the groups given in claim 1 as substituents on Ar and W with the proviso that at least both of the X^1 and X^2 groups or at least both of the Y^1 and Y^2 groups on a given diorganophosphite ligand are groups having a steric hindrance of isopropyl or greater, and with the proviso that no more than three of the X^1, X^2, Y^1 and Y^2 groups are groups having a steric hindrance of isopropyl or greater.

25. A process as defined in claim 24 wherein Z^2 and Z^3 each represent $-OR^6$, R^6 representing C_1-C_{10} alkyl; Y^1 and Y^2 are both branched chain C_3-C_5 alkyl groups; and W is a C_1-C_{10} alkyl group.

26. A process as defined in claim 25 wherein Z^2 and Z^3 each represent methoxy; Y^1 and Y^2 each represent tertiary butyl; and W represents methyl.

27. A process as defined in claim 26 wherein n is zero.

28. A process as defined in claim 23 wherein a ligand having the following formula is prepared:



29. A rhodium complex hydroformylation catalyst comprising rhodium complexed with a diorganophosphite ligand as defined in any one of claims 23 to 28.

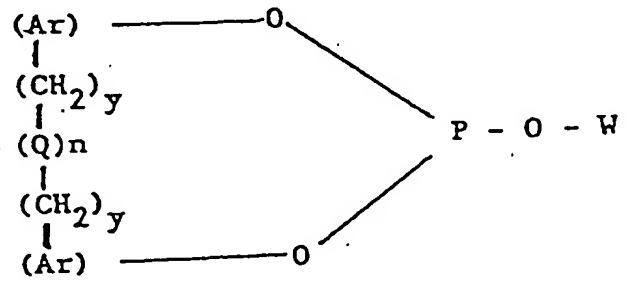
30. A rhodium complex hydroformylation catalytic precursor composition consisting essentially of solubilized rhodium diorganophosphite complex, an organic solvent, and free diorganophosphite ligand, characterized in that the diorganophosphite ligand of said complex and free diorganophosphite ligand is a ligand as defined in claim 1.

31. A composition as defined in claim 30 wherein the rhodium-diorganophosphite complex is a rhodium carbonyl diorganophosphite acetylacetonate complex.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL, SE

1. Hydroformylierungsverfahren zur Herstellung von Aldehyden, welches umfaßt die Umsetzung einer olefinisch ungesättigten organischen Verbindung mit Kohlenmonoxid und Wasserstoff in Anwesenheit eines Rhodiumkomplexkatalysators, der im wesentlichen aus mit Kohlenmonoxid und einem Diorganophosphitliganden komplexiertem Rhodium besteht, und in der zusätzlichen Gegenwart eines freien Diorganophosphitliganden, dadurch gekennzeichnet, daß der mit dem Rhodium komplexierte Diorganophosphitligand und der freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(I)

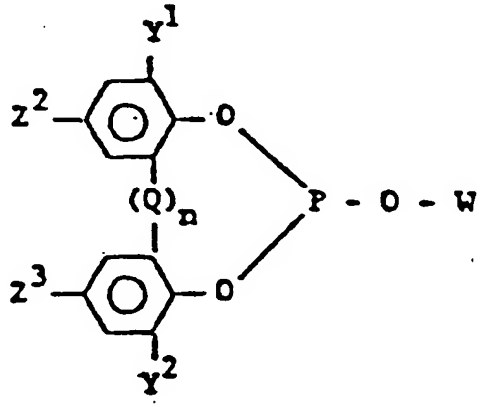
sind,
worin jedes y einzeln einen Wert von 0 oder 1 aufweist;
n einen Wert von 0 oder 1 hat; Q eine zweiwertige Brückengruppe, ausgewählt aus $-CH_2-$, $-CH(CH_3)-$ und -S-, ist;
W eine unsubstituierte oder substituierte C_1-C_{18}-Alkyl- oder eine unsubstituierte oder substituierte C_6-C_{18}-Aryl-Gruppe repräsentiert; und jedes Ar eine identische oder unterschiedliche unsubstituierte oder substituierte Arylgruppe, ausgewählt aus Phenylen, Naphthylen und Anthracylen, darstellt;
wobei der (die) Substituent(en) an W und Ar ausgewählt ist (sind) aus C_1-C_{18}-Alkylgruppen, Phenyl, Naphthyl, Benzyl, Phenylethyl, Tolyl, Xylyl, Cyclopentyl, Cyclohexyl, 1-Methylcyclohexyl, Cyclooctyl, Cyclohexylethyl, Halogen, Nitro, Cyano, Trifluormethyl, Hydroxy, $-Si(R^5)_3$,$-Si(OR^5)_3$, $-N(R^5)_2$, $-C(O)R^5$, $-C(O)OR^5$, $-OC(O)R^6$, $-C(O)N(R^5)_2$, $-N(R^5)C(O)R^5$, $-S(O)_2R^5$, $-S(O)R^5$, $-OR^5$, $-SR^5$, $-P(O)(R^5)_2$, worin R^6 einzeln dieselben oder unterschiedliche Kohlenwasserstoffgruppen darstellt, die aus C_1-C_{18}-Alkylgruppen und Aryl-, Aralkyl-, Alkaryl- und alicyclischen Gruppen, die 6 bis 18 Kohlenstoffatome enthalten, ausgewählt sind, mit der Maßgabe, daß in Substituenten $-N(R^5)_2$ jedes R^5 zusammengenommen auch eine zweiwertige Brückengruppe, die mit dem Stickstoffatom eine heterocyclische Gruppe bildet, darstellen kann, und in Substituenten $-N(R^5)_2$, $-C(O)N(R^5)_2$ und $-N(R^5)C(O)R^5$ jedes an N gebundene R^5 auch Wasserstoff sein kann, während in Substituenten $-P(O)(R^5)_2$ ein R^5 ebenfalls Wasserstoff sein kann; wobei die Ar-Gruppen in Beziehung zu den Sauerstoffatomen, die die Ar-Gruppen mit dem Phosphoratom verbinden, über die ortho-Stellungen gebunden sind; und wobei irgendein Substituent, wenn er an derartigen Ar-Gruppen oder einer Arylgruppe W vorhanden ist, in Beziehung zu dem Sauerstoffatom, das die gegebene substituierte Arylgruppe an das Phosphoratom bindet, in der para- und/oder ortho-Stellung der Arylgruppe gebunden ist,
mit der Maßgabe, daß falls W eine Arylgruppe ist, wenigstens eine der Arylgruppen Ar und W substituiert ist und nicht alle der akkumulativen Gesamtzahl der ortho-Stellungen an Ar und W mit einem Rest substituiert sind, der eine sterische Hinderung von Isopropyl oder größer aufweist.

2. Verfahren wie in Anspruch 1 definiert, worin die olefinisch ungesättigte Verbindung ausgewählt ist aus alpha-Olefinen, die 2 bis 20 Kohlenstoffatome enthalten, internen Olefinen, die 4 bis 20 Kohlenstoffatome enthalten, und Mischungen derartiger alpha- und interner Olefine.

3. Verfahren wie in Anspruch 2 definiert, worin das Olefin-Ausgangsmaterial ausgewählt ist aus Buten-1, Buten-2, Isobutylen und einer Olefinmischung, die im wesentlichen aus Buten-1 und Buten-2 besteht.

4. Verfahren wie in irgendeinem der Ansprüche 1 bis 3 definiert, worin die Hydroformylierungsreaktionsbedingungen eine Reaktionstemperatur im Bereich von 50 bis 120°C, einen Gesamtgasdruck von Wasserstoff, Kohlenmonoxid und olefinisch ungesättigter Verbindung von 6,9 bis 10340 kPa (1 bis 1500 psia), einen Wasserstoffpartialdruck von 100 bis 1100 kPa (15 bis 160 psia), einen Kohlenmonoxidpartialdruck von 6,9 bis 828 kPa (1 bis 120 psia) umfassen und worin das Reaktionsmedium 4 bis 50 Mol des Diorganophosphitliganden pro Mol Rhodium in dem Medium enthält.

5. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin der mit dem Rhodium komplexierte Diorganophosphitligand und der ebenfalls vorhandene freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(II)

sind,
worin Q $-CH_2-$ oder $-CHCH_3-$ darstellt; n 0 oder 1 ist; Y^1, Y^2, Z^2 und Z^3 Wasserstoff oder gleich den Substituenten an Ar und W, die in Anspruch 1 definiert sind, sind, mit der Maßgabe, daß sowohl Y^1 als auch Y^2 Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind; und W eine unsubstituierte C_1-C_{18}-Alkylgruppe darstellt.

6. Verfahren wie in Anspruch 5 definiert, worin Y^1 und Y^2 verzweigte Alkylgruppen mit 3 bis 5 Kohlenstoffatomen sind und worin W eine unsubstituierte C_1-C_{10}-Alkylgruppe darstellt.

7. Verfahren wie in Anspruch 6 definiert, worin Y^1 und Y^2 t-Butylgruppen sind, Q $-CH_2-$ darstellt und W eine unsubstituierte C_1-C_8 Alkylgruppe bedeutet.

8. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin W eine Phosphonyl-substituierte Alkylgruppe der Formel

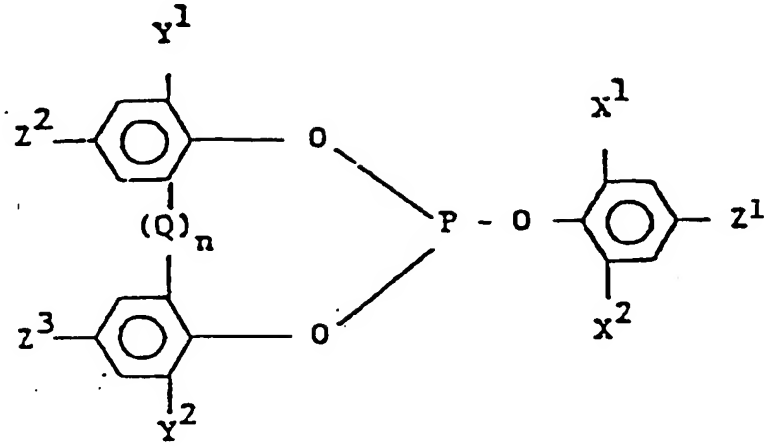
$$-[CR^7)_2]_pP(O)(R^6)_2$$

darstellt, worin jedes R^6 gleich oder verschieden ist und einzeln aus C_1-C_{18}-Alkyl, Phenyl und Cyclohexyl ausgewählt ist; jedes R^7 gleich oder verschieden ist und einzeln aus Wasserstoff und C_1-C_4-Alkyl ausgewählt ist; p eine ganze Zahl von 1 bis 10 ist; mit der Maßgabe, daß ein R^6 auch Wasserstoff sein kann.

9. Verfahren wie in Anspruch 8 definiert, worin W eine $-CH_2CH_2P(O)(C_6H_5)_2$-Gruppe darstellt.

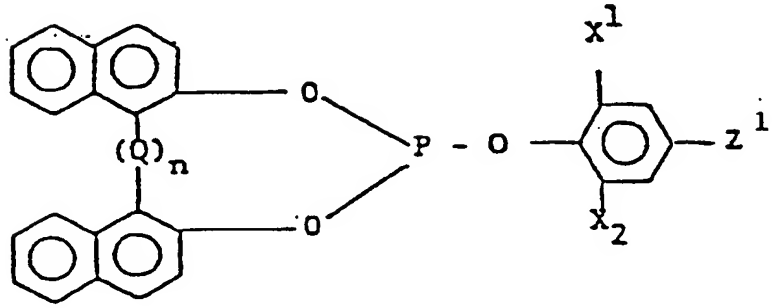
10. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin der mit dem Rhodium komplexierte

Diorganophosphitligand und der ebenfalls vorhandene freie Diorganophosphitligand jeweils einzeln. Liganden mit einer aus



(III)

und

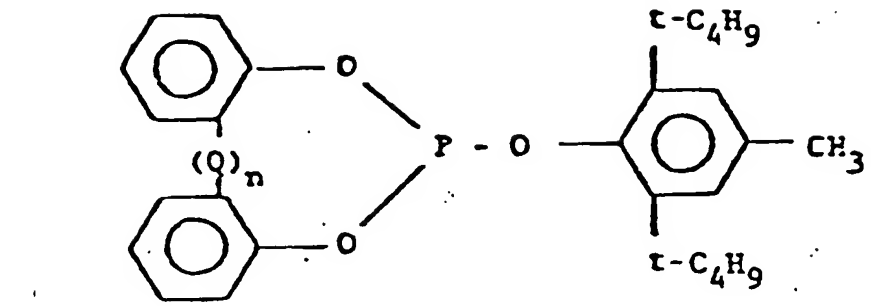


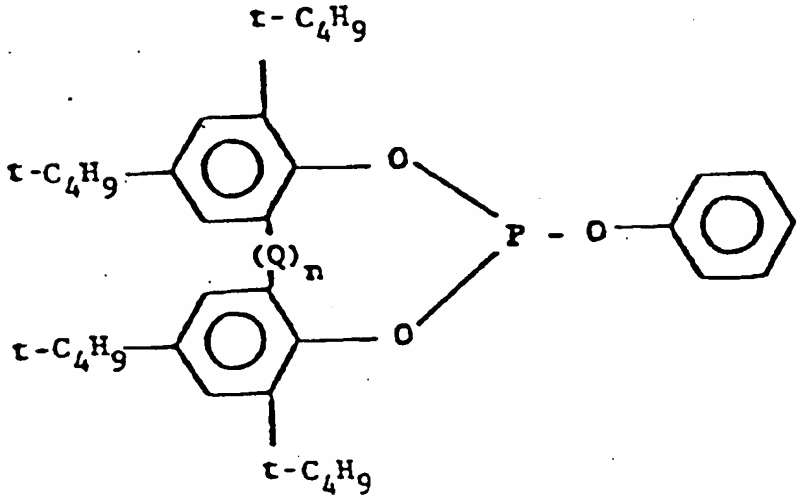
(IV)

ausgewählten Formel sind, worin n einen Wert von 0 oder 1 aufweist; Q $-CH_2-$ oder $-CHCH_3-$ bedeutet; Y^1, Y^2, X^1, X^2, Z^1, Z^2 und Z^3 Wasserstoff darstellen oder die in Anspruch 1 für die Substituenten an W und Ar gegebenen Bedeutungen aufweisen, mit der Maßgabe, daß wenigstens beide der X^1- und X^2-Gruppen oder wenigstens beide der Y^1- und Y^2-Gruppen an einem gegebenen Diorganophosphit der Formeln (III) und (IV) Gruppen sind, die eine sterische Hinderung von Isopropyl oder größer aufweisen, und mit der Maßgabe, daß in Formel (III) nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen sind, die eine sterische Hinderung von Isopropyl oder größer aufweisen.

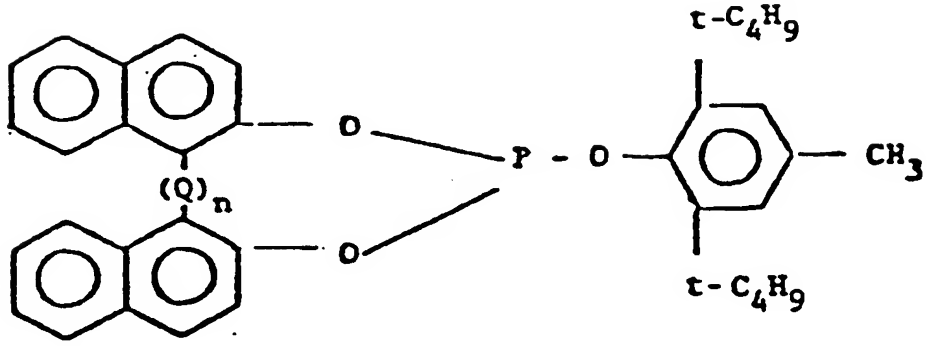
11. Verfahren wie in Anspruch 10 definiert, worin Y^1 und Y^2 verzweigtkettige Alkylgruppen mit 3 bis 5 Kohlenstoffatomen sind.

12. Verfahren wie in Anspruch 10 definiert, worin der Diorganophosphitligand ausgewählt ist aus

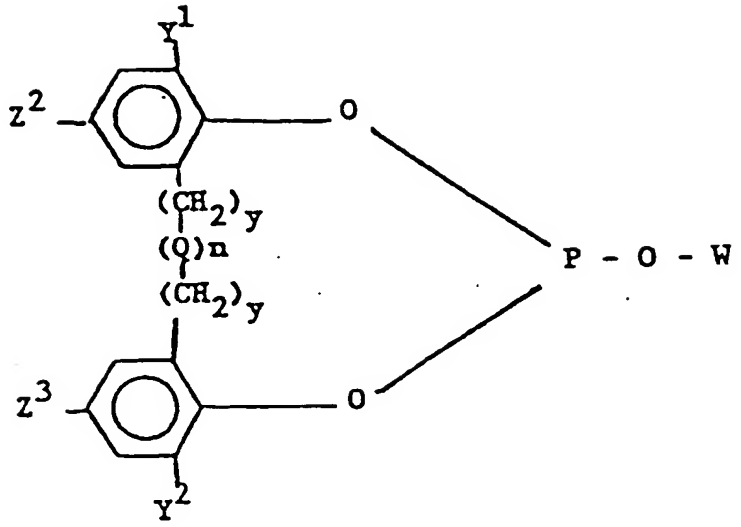




und



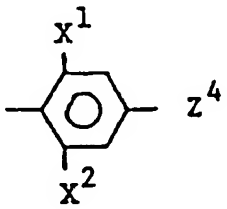
13. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin das mit dem Rhodium komplexierte Diorganophosphit und der ebenfalls anwesende freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(V)

sind, worin Z^2 und Z^3 jeweils einzeln eine Gruppe darstellen, die ausgewählt ist aus Hydroxy und $-OR^6$; y, n, R^6, Q und W gleich wie in Anspruch 1 definiert sind und Y^1, Y^2 Wasserstoff oder irgendeine der Gruppen, die in Anspruch 1 als Substituenten an Ar und W angegeben sind, darstellen.

14. Verfahren wie in Anspruch 13 definiert, worin jedes y einen Wert von 0 hat; Q für $-CH_2-$ oder $-CHCH_3-$ steht; R^6 eine C_1-C_{10}-Alkylgruppe darstellt; Y^1 und Y^2 jeweils einzeln ausgewählt sind aus Wasserstoff, verzweigtkettigen C_3-C_{12}-Alkylgruppen, Phenyl, Benzyl, Cyclohexyl und 1-Methylcyclohexyl; und W ausgewählt ist aus C_1-C_{18}-Alkylgruppen, alpha-Naphthyl, beta-Naphthyl und einer Arylgruppe der Formel



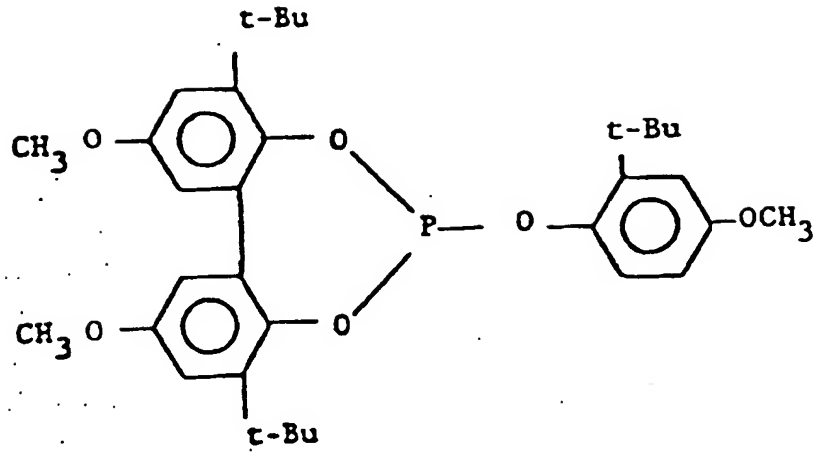
worin X^1, X^2 un Z^4 Wasserstoff oder irgendeine der in Anspruch 1 als Substituenten an Ar und W angegebenen Gruppen darstellen, mit der Maßgabe, daß wenigstens beide der X^1 und X^2-Gruppen oder wenigstens beide der Y^1- und Y^2-Gruppen an einem gegebenen Diorganophosphitliganden Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind, und mit der Maßgabe, daß nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind.

15. Verfahren wie in Anspruch 14 definiert, worin Z^2 und Z^3 jeweils für $-OR^6$ stehen, wobei R^6 C_1-C_{10}-Alkyl darstellt; Y^1 und Y^2 beide verzweigtkettigte C_3-C_5-Alkylgruppen sind; und W eine C_1-C_{10}-Alkylgruppe darstellt.

16. Verfahren wie in Anspruch 15 definiert, worin Z^2 und Z^3 jeweils für Methoxy stehen; Y^1 und Y^2 jeweils für tertiäres Butyl stehen; und W Methyl darstellt.

17. Verfahren wie in Anspruch 15 definiert, worin n 0 ist.

18. Verfahren wie in Anspruch 13 definiert, worin das mit dem Rhodium komplexierte Diorganophosphit und der ebenfalls anwesende freie Diorganophosphitligand



ist.

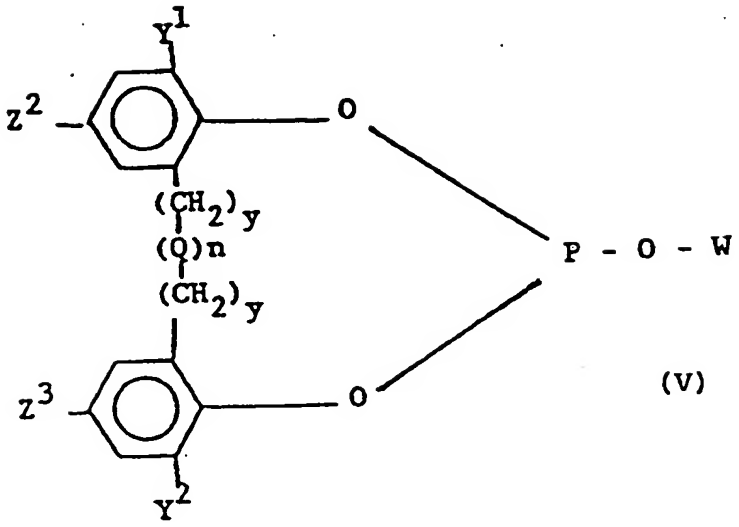
19. Verfahren wie in irgendeinem der Ansprüche 1 bis 18 definiert, welches die Minimierung der Zersetzung des freien Diorganophosphitliganden durch
(a) Entfernung eines Teils des flüssigen Hydroformylierungsreaktionsmediums aus der Hydroformylierungsreaktionszone,
(b) Behandlung des so entfernten flüssigen Mediums mit einem schwach basischen Anionenaustauscherharz,und
(c) Zurückführung des behandelten Reaktionsmediums zur Hydroformylierungsreaktionszone
umfaßt.

20. Verfahren wie in irgendeinem der Ansprüche 1 bis 19 definiert, worin die Hydroformylierung ein kontinuierliches Verfahren für die Recyclisierung der Katalysator enthaltenden Flüssigkeit umfaßt.

21. Verfahren wie in Anspruch 20 definiert, welches die Entfernung eines Teils des flüssigen Hydroformylierungsreaktionsmediums aus der Hydroformylierungsreaktionszone und das Durchleiten des Mediums, entweder vor und/oder nach Abtrennung von Aldehydprodukt daraus, durch ein schwach basisches Anionenaustauscherharzbett umfaßt.

22. Verfahren wie in irgendeinem der Ansprüche 19 bis 21 definiert, worin das schwach basische Anionenaustauscherharz ein vernetztes tertiäres Amin-Polystyrol-Anionenaustauscherharz vom Gel- oder makroretikulären Typ umfaßt.

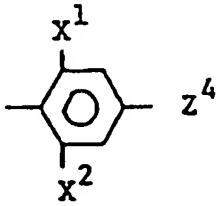
23. Diorganophosphitligand mit der allgemeinen Formel



(V)

worin Z^2 und Z^3 jeweils einzeln eine Gruppe darstellen, die ausgewahlt ist aus Hydroxy und $-OR^6$; y, n, R^6, Q und W gleich wie in Anspruch 1 definiert sind und Y^1, Y^2 Wasserstoff oder irgendeine der in Anspruch 1 als Substituenten an Ar und W angegebenen Gruppen sind, mit der Maßgabe, daß falls W eine substituierte Arylgruppe ist, der (die) Substituent(en) in Beziehung zum Sauerstoffatom, das die Arylgruppe an das Phosphoratom bindet, an die para- und/oder ortho-Stellung der Arylgruppe gebunden ist (sind), und auch mit der Maßgabe, daß wenigstens eines von Y^1, Y^2, Z^2 und Z^3 und der Substituenten an einer Arylgruppe W, falls vorhanden, von Wasserstoff verschieden ist und nicht alle der gesamten verfügbaren ortho-Stellungen an den vorhandenen Arylgruppen eine sterische Hinderung von Isopropyl oder größer aufweisen.

24. Diorganophosphitligand wie in Anspruch 23 definiert, worin jedes Y einen Wert von 0 hat; Q für $-CH_2-$ oder $-CHCH_3-$ steht; R^6 eine C_1-C_{10}-Alkylgruppe ist; Y^1 und Y^2 jeweils einzeln ausgewählt sind aus Wasserstoff, verzweigtkettigen C_3-C_{12}-Alkylgruppen, Phenyl, Benzyl, Cyclohexyl und 1-Methylcyclohexyl; und W ausgewählt ist aus C_1-C_{18}-Alkylgruppen, alpha-Naphthyl, beta-Naphthyl und einer Arylgruppe der Formel



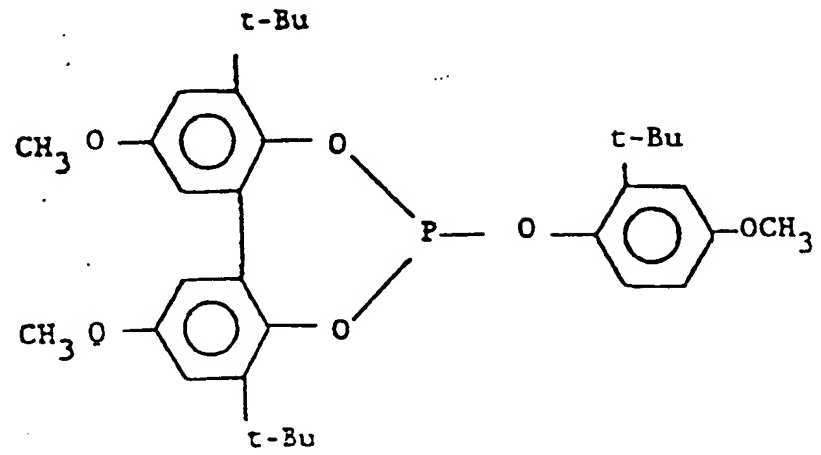
worin X^1, X^2 und Z^4 Wasserstoff oder irgendeine der Gruppen, die in Anspruch 1 als Substituenten an Ar und W angegeben sind, sind, mit der Maßgabe, daß wenigstens beide der X^1- und X^2-Gruppen oder wenigstens beide der Y^1-und Y^2-Gruppen an einem gegebenen Diorganophosphitliganden Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind, und mit der Maßgabe, daß nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind.

25. Ligand wie in Anspruch 24 definiert, worin Z^2 und Z^3 jeweils für $-OR^6$ stehen, wobei R^6 C_1-C_{10}-Alkyl darstellt; Y^1 nd Y^2 beide verzweigtkettige C_3-C_5-Alkylgruppen sind; und W eine C_1-C_{10}-Alkylgruppe ist.

26. Ligand wie in Anspruch 25 definiert, worin Z^2 und Z^3 jeweils für Methoxy stehen; Y^1 und Y^2 jeweils für tertiäres Butyl stehen; und W Methyl darstellt.

27. Ligand wie in Anspruch 26 definiert, worin n 0 ist.

28. Ligand wie in Anspruch 23 definiert, mit der Formel:



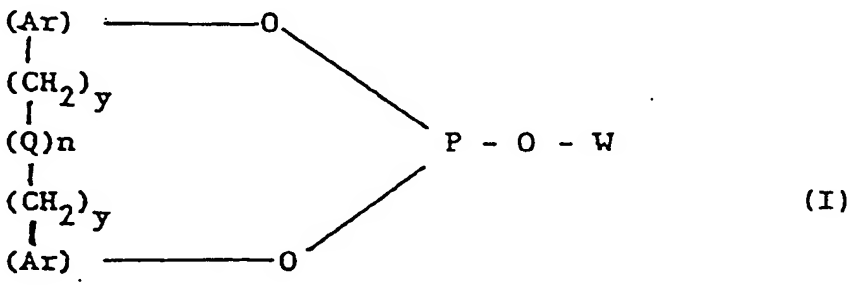
29. Rhodiumkomplex-Hydroformylierungskatalysator, umfassend Rhodium, komplexiert mit einem Diorganophosphitliganden wie in irgendeinem der Ansprüche 23 bis 28 definiert.

30. Rhodiumkomplex-Hydroformylierungskatalysator-Vorläuferzusammensetzung, im wesentlichen bestehend aus löslich gemachtem Rhodium-Diorganophosphit-Komplex, einem organischen Lösungsmittel und einem freien Diorganophosphitliganden, dadurch gekennzeichnet, daß der Diorganophosphitligand des Komplexes und der freie Diorganophosphitligand ein Ligand wie in Anspruch 1 definiert ist.

31. Zusammensetzung wie in Anspruch 30 definiert, worin der Rhodium-Diorganophosphit-Komplex ein Rhodiumcarbonyldiorganophosphitacetylacetonat-Komplex ist.

Patentansprüche für folgenden Vertragsstaat : AT

1. Hydroformylierungsverfahren zur Herstellung von Aldehyden, welches umfaßt die Umsetzung einer olefinisch ungesättigten organischen Verbindung mit Kohlenmonoxid und Wasserstoff in Anwesenheit eines Rhodiumkomplexkatalysators, der im wesentlichen aus mit Kohlenmonoxid und einem Diorganophosphitliganden komplexiertem Rhodium besteht, und in der zusätzlichen Gegenwart eines freien Diorganophosphitliganden, dadurch gekennzeichnet, daß der mit dem Rhodium komplexierte Diorganophosphitligand und der freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(I)

sind,
worin jedes y einzeln einen Wert von 0 oder 1 aufweist;
n einen Wert von 0 oder 1 hat; Q eine zweiwertige Brükkengruppe, ausgewählt aus $-CH_2-$, $-CH(CH_3)-$ und -S-, ist;
W eine unsubstituierte oder substituierte C_1-C_{18}-Alkyl- oder eine unsubstituierte oder substituierte C_6-

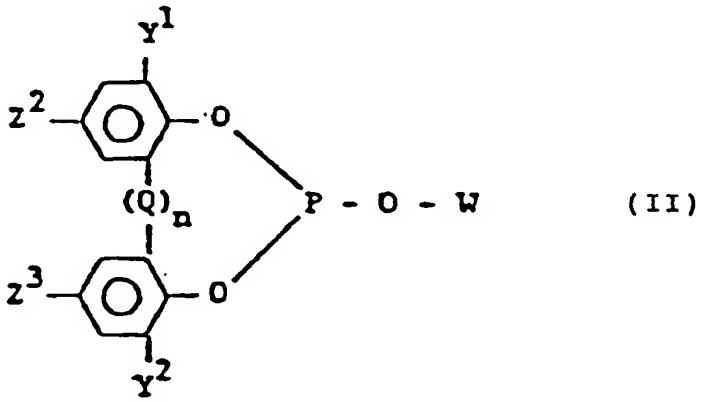
C_{18}-Aryl-Gruppe repräsentiert; und jedes Ar eine identische oder unterschiedliche unsubstituierte oder substituierte Arylgruppe, ausgewählt aus Phenylen, Naphthylen und Anthracylen, darstellt;
wobei der (die) Substituent(en) an W und Ar ausgewählt ist (sind) aus C_1-C_{18}-Alkylgruppen, Phenyl, Naphthyl, Benzyl, Phenylethyl, Tolyl, Xylyl, Cyclopentyl, Cyclohexyl, 1-Methylcyclohexyl, Cyclooctyl, Cyclohexylethyl, Halogen, Nitro, Cyano, Trifluormethyl, Hydroxy, $-Si(R^6)_3$,$-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$, $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$, worin R^6 einzeln dieselben oder unterschiedliche Kohlenwasserstoffgruppen darstellt, die aus C_1-C_{18}-Alkylgruppen und Aryl-, Aralkyl-, Alkaryl- und alicyclischen Gruppen, die 6 bis 18 Kohlenstoffatome enthalten, ausgewählt sind, mit der Maßgabe, daß in Substituenten $-N(R^6)_2$ jedes R^6 zusammengenommen auch eine zweiwertige Brückengruppe, die mit dem Stickstoffatom eine heterocyclische Gruppe bildet, darstellen kann, und in Substituenten $-N(R^6)_2$, $-C(O)N(R^6)_2$ und $-N(R^6)C(O)R^6$ jedes an N gebundene R^6 auch Wasserstoff sein kann, während in Substituenten $-P(O)(R^6)_2$ ein R^6 ebenfalls Wasserstoff sein kann; wobei die Ar-Gruppen in Beziehung zu den Sauerstoffatomen, die die Ar-Gruppen mit dem Phosphoratom verbinden, über die ortho-Stellungen gebunden sind; und wobei irgendein Substituent, wenn er an derartigen Ar-Gruppen oder einer Arylgruppe W vorhanden ist, in Beziehung zu dem Sauerstoffatom, das die gegebene substituierte Arylgruppe an das Phosphoratom bindet, in der para- und/oder ortho-Stellung der Arylgruppe gebunden ist,
mit der Maßgabe, daß falls W eine Arylgruppe ist, wenigstens eine der Arylgruppen Ar und W substituiert ist und nicht alle der akkumulativen Gesamtzahl der ortho-Stellungen an Ar und W mit einem Rest substituiert sind, der eine sterische Hinderung von Isopropyl oder größer aufweist.

2. Verfahren wie in Anspruch 1 definiert, worin die olefinisch ungesättigte Verbindung ausgewählt ist aus alpha-Olefinen, die 2 bis 20 Kohlenstoffatome enthalten, internen Olefinen, die 4 bis 20 Kohlenstoffatome enthalten, und Mischungen derartiger alpha- und interner Olefine.

3. Verfahren wie in Anspruch 2 definiert, worin das Olefin-Ausgangsmaterial ausgewählt ist aus Buten-1, Buten-2, Isobutylen und einer Olefinmischung, die im wesentlichen aus Buten-1 und Buten-2 besteht.

4. Verfahren wie in irgendeinem der Ansprüche 1 bis 3 definiert, worin die Hydroformylierungsreaktionsbedingungen eine Reaktionstemperatur im Bereich von 50 bis 120°C, einen Gesamtgasdruck von Wasserstoff, Kohlenmonoxid und olefinisch ungesättigter Verbindung von 6,9 bis 10340 kPa (1 bis 1500 psia), einen Wasserstoffpartialdruck von 100 bis 1100 kPa (15 bis 160 psia), einen Kohlenmonoxidpartialdruck von 6,9 bis 828 kPa (1 bis 120 psia) umfassen und worin das Reaktionsmedium 4 bis 50 Mol des Diorganophosphitliganden pro Mol Rhodium in dem Medium enthält.

5. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin der mit dem Rhodium komplexierte Diorganophosphitligand und der ebenfalls vorhandene freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(II)

sind,
worin Q $-CH_2-$ oder $-CHCH_3-$ darstellt; n 0 oder 1 ist; Y^1, Y^2, Z^2 und Z^3 Wasserstoff oder gleich den Substituenten an Ar und W, die in Anspruch 1 definiert sind, sind, mit der Maßgabe, daß sowohl Y^1 als

auch Y^2 Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind; und W eine unsubstituierte C_1-C_{18}-Alkylgruppe darstellt.

6. Verfahren wie in Anspruch 5 definiert, worin Y^1 und Y^2 verzweigte Alkylgruppen mit 3 bis 5 Kohlenstoffatomen sind und worin W eine unsubstituierte C_1-C_{10}-Alkylgruppe darstellt.

7. Verfahren wie in Anspruch 6 definiert, worin Y^1 und Y^2 t-Butylgruppen sind, Q $-CH_2-$ darstellt und W eine unsubstituierte C_1-C_8 Alkylgruppe bedeutet.

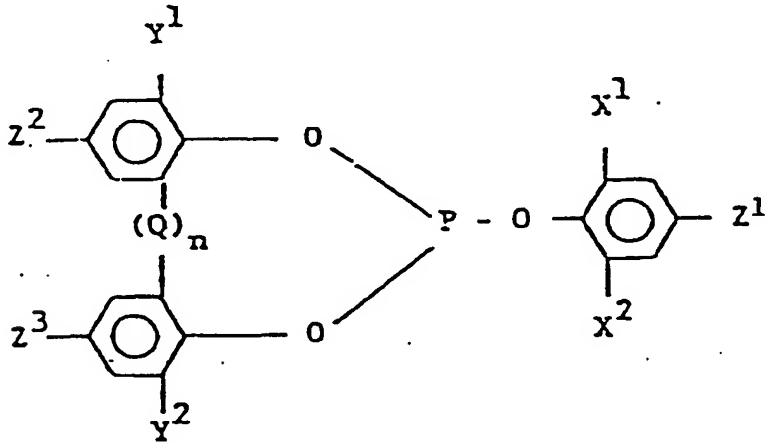
8. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin W eine Phosphonyl-substituierte Alkylgruppe der Formel

$$-[CR^7)_2]_pP(O)(R^6)_2$$

darstellt, worin jedes R^6 gleich oder verschieden ist und einzeln aus C_1-C_{18}-Alkyl, Phenyl und Cyclohexyl ausgewählt ist; jedes R^7 gleich oder verschieden ist und einzeln aus Wasserstoff und C_1-C_4-Alkyl ausgewählt ist; p eine ganze Zahl von 1 bis 10 ist; mit der Maßgabe, daß ein R^6 auch Wasserstoff sein kann.

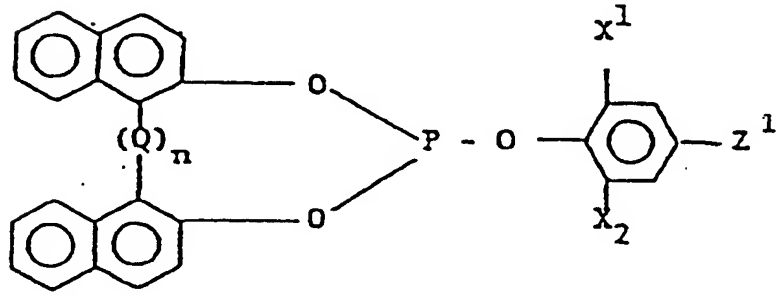
9. Verfahren wie in Anspruch 8 definiert, worin W eine $-CH_2CH_2P(O)(C_6H_5)_2$-Gruppe darstellt.

10. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin der mit dem Rhodium komplexierte Diorganophosphitligand und der ebenfalls vorhandene freie Diorganophosphitligand jeweils einzeln Liganden mit einer aus



(III)

und



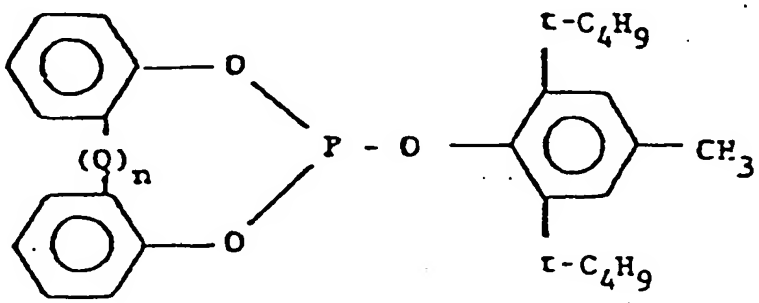
(IV)

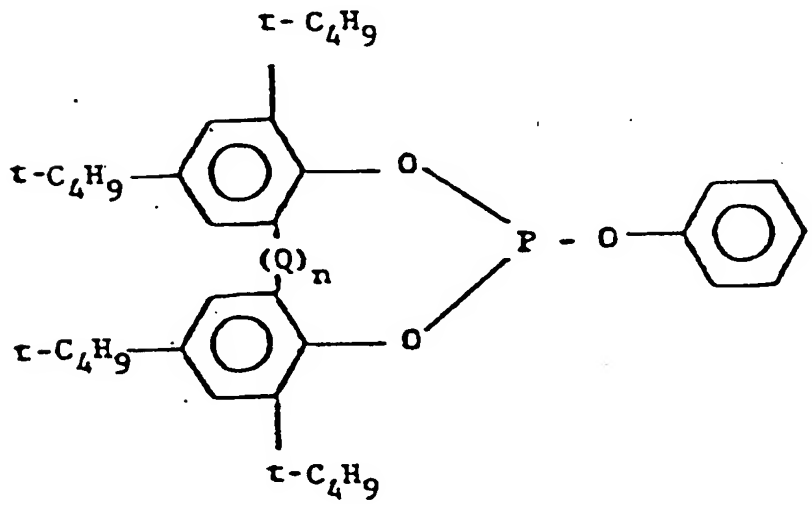
ausgewählten Formel sind, worin n einen Wert von 0 oder 1 aufweist; Q $-CH_2-$ oder $-CHCH_3-$ bedeutet; Y^1, Y^2, X^1, X^2, Z^1, Z^2 und Z^3 Wasserstoff darstellen oder die in Anspruch 1 für die Substituenten an W

und Ar gegebenen Bedeutungen aufweisen, mit der Maßgabe, daß wenigstens beide der X^1- und X^2-Gruppen oder wenigstens beide der Y^1- und Y^2-Gruppen an einem gegebenen Diorganophosphit der Formeln (III) und (IV) Gruppen sind, die eine sterische Hinderung von Isopropyl oder größer aufweisen, und mit der Maßgabe, daß in Formel (III) nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen sind, die eine sterische Hinderung von Isopropyl oder größer aufweisen.

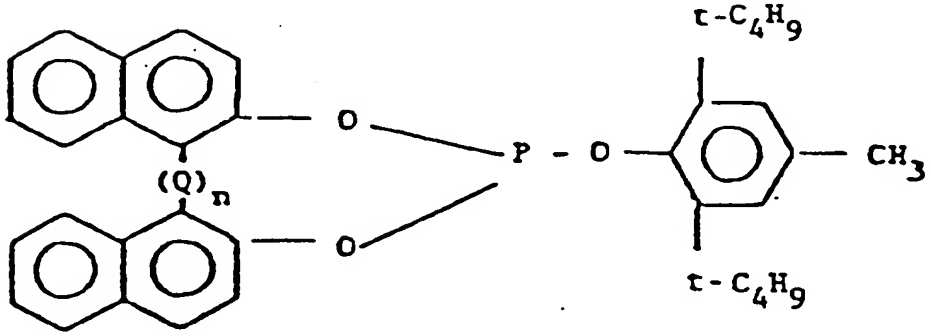
11. Verfahren wie in Anspruch 10 definiert, worin Y^1 und Y^2 verzweigtkettige Alkylgruppen mit 3 bis 5 Kohlenstoffatomen sind.

12. Verfahren wie in Anspruch 10 definiert, worin der Diorganophosphitligand ausgewählt ist aus



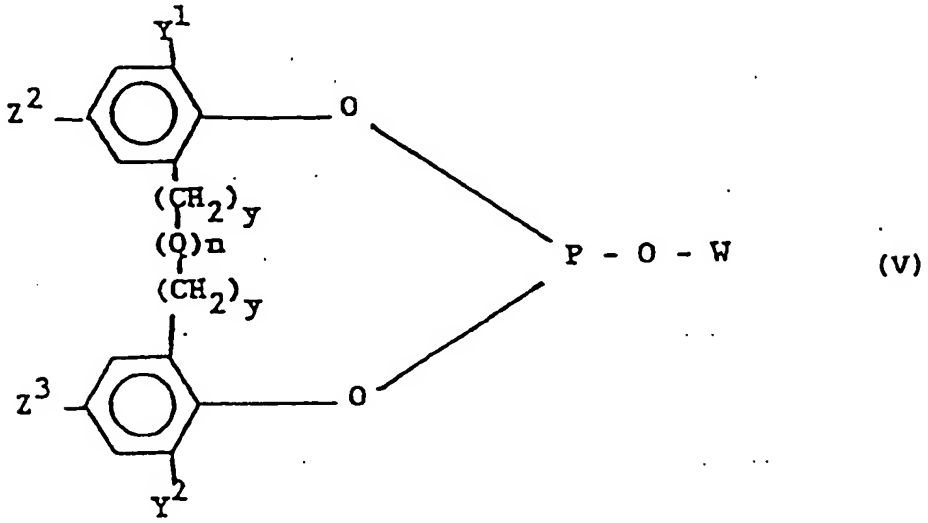


und



13. Verfahren wie in irgendeinem der Ansprüche 1 bis 4 definiert, worin das mit dem Rhodium komplexier-

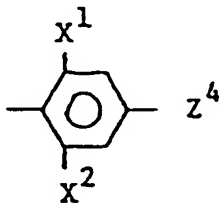
te Diorganophosphit und der ebenfalls anwesende freie Diorganophosphitligand jeweils einzeln Liganden mit der Formel



(V)

sind, worin Z^2 und Z^3 jeweils einzeln eine Gruppe darstellen, die ausgewählt ist aus Hydroxy und $-OR^6$; y, n, R^6, Q und W gleich wie in Anspruch 1 definiert sind und Y^1, Y^2 Wasserstoff oder irgendeine der Gruppen, die in Anspruch 1 als Substituenten an Ar und W angegeben sind, darstellen.

14. Verfahren wie in Anspruch 13 definiert, worin jedes y einen Wert von 0 hat; Q für $-CH_2-$ oder $-CHCH_3-$ steht; R^6 eine C_1-C_{10}-Alkylgruppe darstellt; Y^1 und Y^2 jeweils einzeln ausgewählt sind aus Wasserstoff, verzweigtkettigen C_3-C_{12}-Alkylgruppen, Phenyl, Benzyl, Cyclohexyl und 1-Methylcyclohexyl; und W ausgewählt ist aus C_1-C_{18}-Alkylgruppen, alpha-Naphthyl, beta-Naphthyl und einer Arylgruppe der Formel



worin X^1, X^2 un Z^4 Wasserstoff oder irgendeine der in Anspruch 1 als Substituenten an Ar und W angegebenen Gruppen darstellen, mit der Maßgabe, daß wenigstens beide der X^1 und X^2-Gruppen oder wenigstens beide der Y^1- und Y^2-Gruppen an einem gegebenen Diorganophosphitliganden Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind, und mit der Maßgabe, daß nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind.

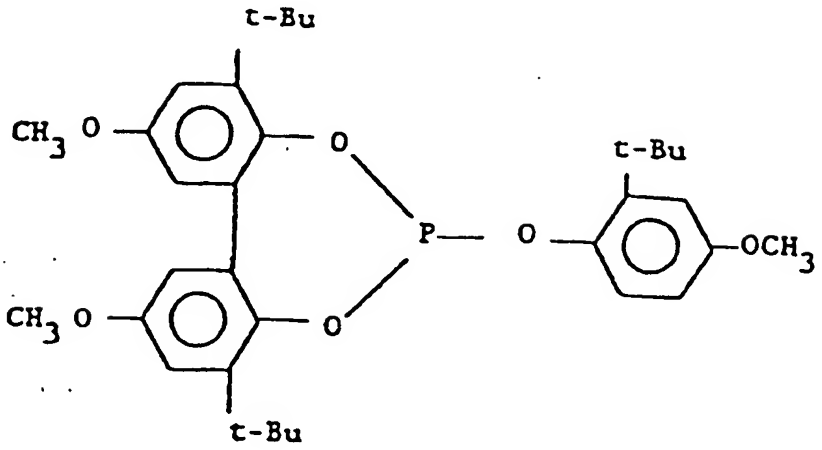
15. Verfahren wie in Anspruch 14 definiert, worin Z^2 und Z^3 jeweils für $-OR^6$ stehen, wobei R^6 C_1-C_{10}-Alkyl darstellt; Y^1 und Y^2 beide verzweigtkettigte C_3-C_5-Alkylgruppen sind; und W eine C_1-C_{10}-Alkylgruppe darstellt.

16. Verfahren wie in Anspruch 15 definiert, worin Z^2 und Z^3 jeweils für Methoxy stehen; Y^1 und Y^2 jeweils für tertiäres Butyl stehen; und W Methyl darstellt.

17. Verfahren wie in Anspruch 15 definiert, worin n 0 ist.

18. Verfahren wie in Anspruch 13 definiert, worin das mit dem Rhodium komplexierte Diorganophosphit und

der ebenfalls anwesende freie Diorganophosphitligand



ist.

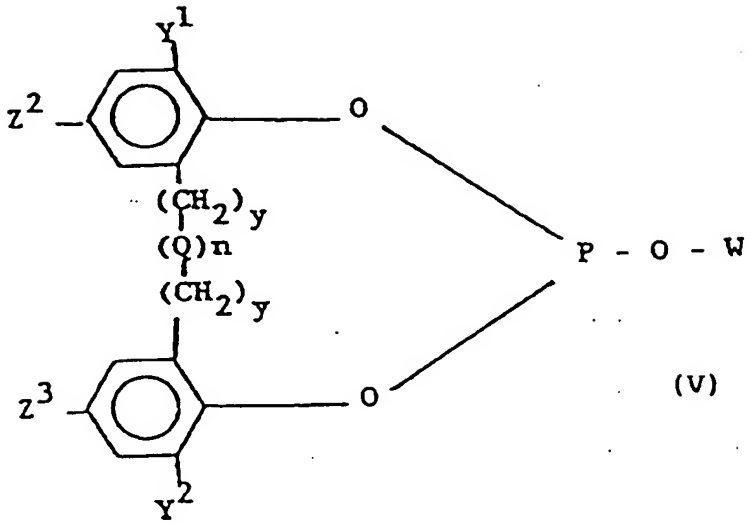
19. Verfahren wie in irgendeinem der Ansprüche 1 bis 18 definiert, welches die Minimierung der Zersetzung des freien Diorganophosphitliganden durch
(a) Entfernung eines Teils des flüssigen Hydroformylierungsreaktionsmediums aus der Hydroformylierungsreaktionszone,
(b) Behandlung des so entfernten flüssigen Mediums mit einem schwach basischen Anionenaustauscherharz,und
(c) Zurückführung des behandelten Reaktionsmediums zur Hydroformylierungsreaktionszone
umfaßt.

20. Verfahren wie in irgendeinem der Ansprüche 1 bis 19 definiert, worin die Hydroformylierung ein kontinuierliches Verfahren für die Recyclisierung der Katalysator enthaltenden Flüssigkeit umfaßt.

21. Verfahren wie in Anspruch 20 definiert, welches die Entfernung eines Teils des flüssigen Hydroformylierungsreaktionsmediums aus der Hydroformylierungsreaktionszone und das Durchleiten des Mediums, entweder vor und/oder nach Abtrennung von Aldehydprodukt daraus, durch ein schwach basisches Anionenaustauscherharzbett umfaßt.

22. Verfahren wie in irgendeinem der Ansprüche 19 bis 21 definiert, worin das schwach basische Anionenaustauscherharz ein vernetztes tertiäres Amin-Polystyrol-Anionenaustauscherharz vom Gel- oder makroretikulären Typ umfaßt.

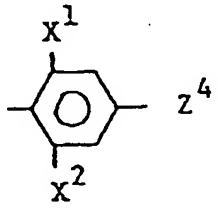
23. Verfahren zur Herstellung eines Diorganophosphitliganden mit der allgemeinen Formel



(V)

worin Z^2 und Z^3 jeweils einzeln eine Gruppe darstellen, die ausgewählt ist aus Hydroxy und $-OR^6$; y, n, R^6, Q und W gleich wie in Anspruch 1 definiert sind und Y^1, Y^2 Wasserstoff oder irgendeine der in Anspruch 1 als Substituenten an Ar und W angegebenen Gruppen sind, mit der Maßgabe, daß falls W eine substituierte Arylgruppe ist, der (die) Substituent(en) in Beziehung zum Sauerstoffatom, das die Arylgruppe an das Phosphoratom bindet, an die para- und/oder ortho-Stellung der Arylgruppe gebunden ist (sind), und auch mit der Maßgabe, daß wenigstens eines von Y^1, Y^2, Z^2 und Z^3 und der Substituenten an einer Arylgruppe W, falls vorhanden, von Wasserstoff verschieden ist und nicht alle der gesamten verfügbaren ortho-Stellungen an den vorhandenen Arylgruppen eine sterische Hinderung von Isopropyl oder größer aufweisen, welches Verfahren umfaßt die Umsetzung einer entsprechenden organischen Diphenol-Verbindung mit Phosphortrichlorid, um ein organisches Phosphorochloridit-Zwischenprodukt zu bilden, das wiederum in Anwesenheit eines HCl-Akzeptors mit einer entsprechenden Monohydroxyverbindung umgesetzt wird, um den gewünschten Diorganophosphitliganden zu erzeugen.

24. Verfahren wie in Anspruch 23 definiert, worin Y einen Wert von 0 hat; Q für $-CH_2-$ oder $-CHCH_3-$ steht; R^6 eine C_1-C_{10}-Alkylgruppe ist; Y^1 und Y^2 jeweils einzeln ausgewählt sind aus Wasserstoff, verzweigtkettigen C_3-C_{12}-Alkylgruppen, Phenyl, Benzyl, Cyclohexyl und 1-Methylcyclohexyl; und W ausgewählt ist aus C_1-C_{18}-Alkylgruppen, alpha-Naphthyl, beta-Naphthyl und einer Arylgruppe der Formel



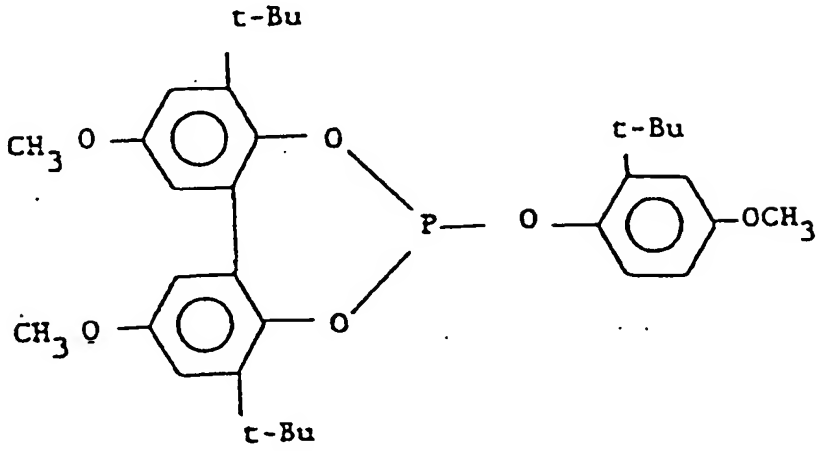
worin X^1, X^2 und Z^4 Wasserstoff oder irgendeine der Gruppen, die in Anspruch 1 als Substituenten an Ar und W angegeben sind, sind, mit der Maßgabe, daß wenigstens beide der X^1- und X^2-Gruppen oder wenigstens beide der Y^1-und Y^2-Gruppen an einem gegebenen Diorganophosphitliganden Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind, und mit der Maßgabe, daß nicht mehr als drei der X^1-, X^2-, Y^1- und Y^2-Gruppen Gruppen mit einer sterischen Hinderung von Isopropyl oder größer sind.

25. Verfahren wie in Anspruch 24 definiert, worin Z^2 und Z^3 jeweils für $-OR^6$ stehen, wobei R^6 C_1-C_{10}-Alkyl darstellt; Y^1 nd Y^2 beide verzweigtkettige C_3-C_5-Alkylgruppen sind; und W eine C_1-C_{10}-Alkylgruppe ist.

26. Verfahren wie in Anspruch 25 definiert, worin Z^2 und Z^3 jeweils für Methoxy stehen; Y^1 und Y^2 jeweils für tertiäres Butyl stehen; und W Methyl darstellt.

27. Verfahren wie in Anspruch 26 definiert, worin n 0 ist.

28. Verfahren wie in Anspruch 23 definiert, worin ein Ligand mit der Formel:



hergestellt wird.

29. Rhodiumkomplex-Hydroformylierungskatalysator, umfassend Rhodium, komplexiert mit einem Diorganophosphitliganden wie in irgendeinem der Ansprüche 23 bis 28 definiert.

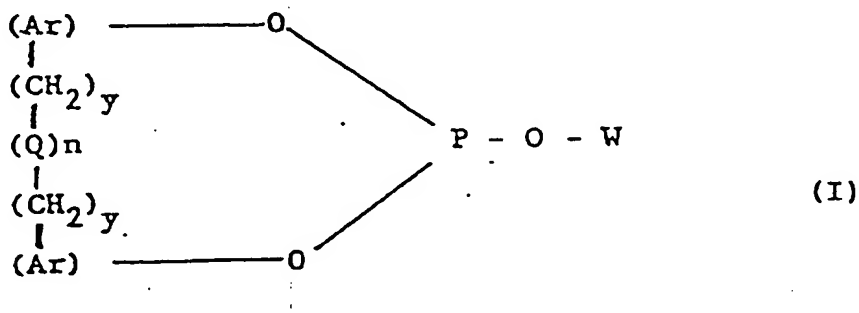
30. Rhodiumkomplex-Hydroformylierungskatalysator-Vorläuferzusammensetzung, im wesentlichen bestehend aus löslich gemachtem Rhodium-Diorganophosphit-Komplex, einem organischen Lösungsmittel und einem freien Diorganophosphitliganden, dadurch gekennzeichnet, daß der Diorganophosphitligand des Komplexes und der freie Diorganophosphitligand ein Ligand wie in Anspruch 1 definiert ist.

31. Zusammensetzung wie in Anspruch 30 definiert, worin der Rhodium-Diorganophosphit-Komplex ein Rhodiumcarbonyldiorganophosphitacetylacetonat-Komplex ist.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL, SE

1. Procédé d'hydroformylation pour la production d'aldéhydes, qui consiste à faire réagir un composé organique à non-saturation oléfinique avec l'oxyde de carbone et l'hydrogène en présence d'un catalyseur à base d'un complexe de rhodium essentiellement constitué de rhodium complexé avec de l'oxyde de carbone et un ligand diorganophosphitique, et en présence d'une addition d'un ligand diorganophosphitique libre, caractérisé en ce que le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre sont tous deux, individuellement, des ligands répondant à la formule



(I)

dans laquelle chaque y a individuellement la valeur 0 ou 1 ;

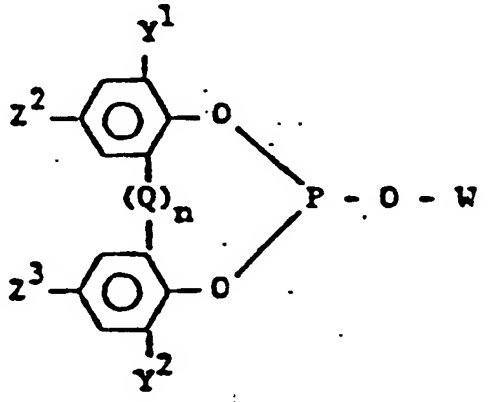
n a la valeur 0 ou 1 ; Q est un groupe divalent de pontage choisi entre $-CH_2-$, $-CH(CH_3)-$ et -S- ;
W est un groupe alkyle en C_1 à C_{18} non substitué ou substitué ou un groupe aryle en C_6 à C_{18} non substitué ou substitué ; et chaque Ar représente des groupes aryle non substitués ou substitués identiques ou différents choisis entre les groupes phénylène, naphtylène et anthracylène ;
le ou les substituants portés par W et Ar étant choisis entre des groupes alkyle en C_1 à C_{18}, phényle, naphtyle, benzyle, phényléthyle, tolyle, xylyle, cyclopentyle, cyclohexyle, 1-méthylcyclohexyle, cyclooctyle, cyclohexyléthyle, halogéno, nitro, cyano, trifluorométhyle, hydroxy, $-Si(R^6)_3$, $-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$, $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$ où R^6 représente individuellement des groupes hydrocarbyle identiques ou différents choisis entre des groupes alkyle en C_1 à C_{18} et des groupes aryle, aralkyle, alkaryle et alicycliques contenant 6 à 18 atomes de carbone, sous réserve que dans des substituants $-N(R^6)_2$, les groupes R^6 pris conjointement puissent aussi représenter un groupe divalent de pontage qui forme un groupe hétérocyclique avec l'atome d'azote et que, dans les substituants $-N(R^6)_2$, $-C(O)N(R^6)_2$ et $-N(R^6)C(O)R^6$, les groupes R^6 liés à l'azote puissent aussi représenter de l'hydrogène tandis que, dans les substituants $-P(O)(R^6)_2$, un groupe R^6 puisse aussi représenter l'hydrogène ; les groupes Ar étant liés dans les positions ortho par rapport aux atomes d'oxygène qui lient les groupes Ar à l'atome de phosphore ; et tout substituant, présent sur de tels groupes Ar ou sur un groupe aryle W, étant lié dans la position para et/ou dans la position ortho du groupe aryle par rapport à l'atome d'oxygène qui lie le groupe aryle substitué en question à l'atome de phosphore,
sous réserve que lorsque W est un groupe aryle, l'un au moins desdits groupes aryle Ar et W soit substitué et que le nombre total cumulatif de positions ortho sur Ar et W ne soit pas en totalité substitué avec un radical possédant un encombrement stérique d'isopropyle ou supérieur.

2. Procédé suivant la revendication 1, dans lequel le composé à non-saturation oléfinique est choisi entre des alpha-oléfines contenant 2 à 20 atomes de carbone, des oléfines internes contenant 4 à 20 atomes de carbone et des mélanges de ces alpha-oléfines et de ces oléfines internes.

3. Procédé suivant la revendication 2, dans lequel l'oléfine de départ est choisie entre le butène-1, le butène-2, l'isobutylène et un mélange d'oléfines essentiellement constitué de butène-1 et de butène-2.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel les conditions de la réaction d'hydroformylation comprennent une température de réaction dans la plage de 50 à 120°C, une pression absolue totale du gaz formé d'hydrogène, d'oxyde de carbone et de composé organique à non-saturation oléfinique de 6,9 à 10 340 kPa (1 à 1500 lb/in^2), une pression absolue partielle d'hydrogène de 100 à 1100 kPa (15 à 160 lb/in^2), une pression absolue partielle d'oxyde de carbone de 6,9 à 828 kPa (1 à 120 lb/in^2), et le milieu réactionnel contient 4 à 50 moles dudit ligand diorganophosphitique par mole de rhodium dans ledit milieu.

5. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands répondant à la formule



(II)

dans laquelle Q est un groupe $-CH_2-$ ou $-CHCH_3-$; n a la valeur 0 ou 1 ; Y^1, Y^2, Z^2 et Z^3 sont de

l'hydrogène ou sont identiques aux substituants portés par Ar et W définis dans la revendication 1, sous réserve que Y^1 er Y^2 soient tous deux des groupes ayant un encombrement stérique d'isopropyle ou supérieur ; et W représente un groupe alkyle en C_1 à C_{18} non substitué.

6. Procédé suivant la revendication 5, dans lequel Y^1 et Y^2 sont des groupes alkyle ramifiés ayant 3 à 5 atomes de carbone et W est un groupe alkyle en C_1 à C_{10} non substitué.

7. Procédé suivant la revendication 6, dans lequel Y^1 et Y^2 sont des groupes tertiobutyle, Q est un groupe $-CH_2-$ et W est un groupe alkyle en C_1 à C_8 non substitué.

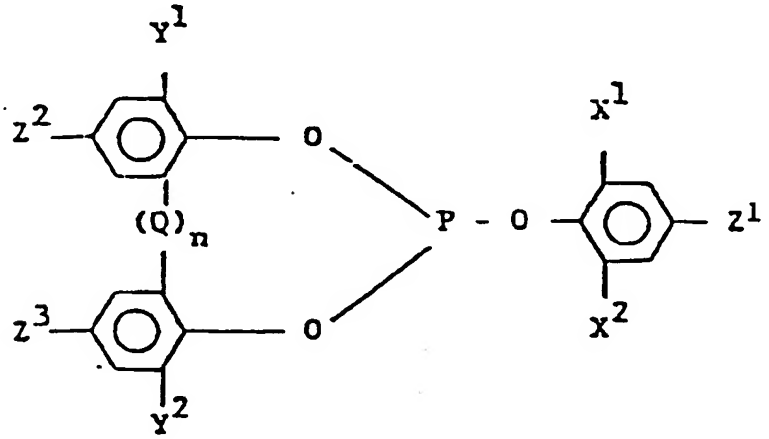
8. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel W est un groupe alkyle à substituant phosphonyle de formule

$$-[C(R^7)_2]_pP(O)(R^6)_2$$

dans laquelle les groupes R^6 sont identiques ou différents et sont choisis individuellement entre des groupes alkyle en C_1 à C_{18}, phényle et cyclohexyle ; les groupes R^7 sont identiques ou différents et chacun est choisi individuellement entre l'hydrogène et des groupes alkyle en C_1 à C_4 ; p est un nombre entier de 1 à 10 ; sous réserve que l'un des groupes R^6 puisse aussi représenter l'hydrogène.

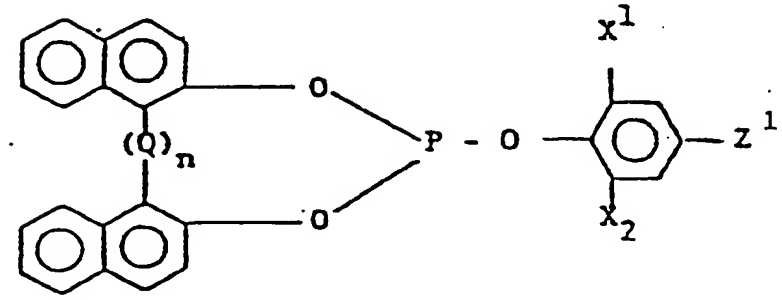
9. Procédé suivant la revendication 8, dans lequel W est un groupe $-CH_2CH_2P(O)(C_6H_5)_2$.

10. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands ayant une formule choisie entre



(III)

et



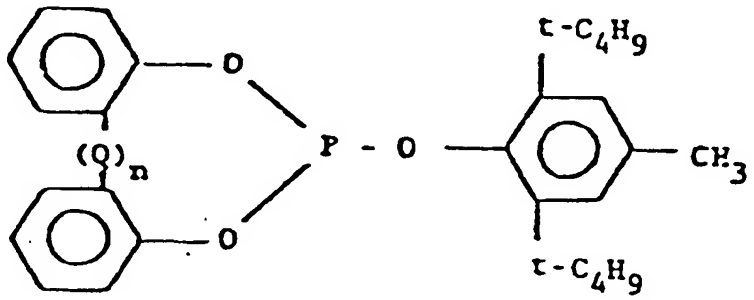
(IV)

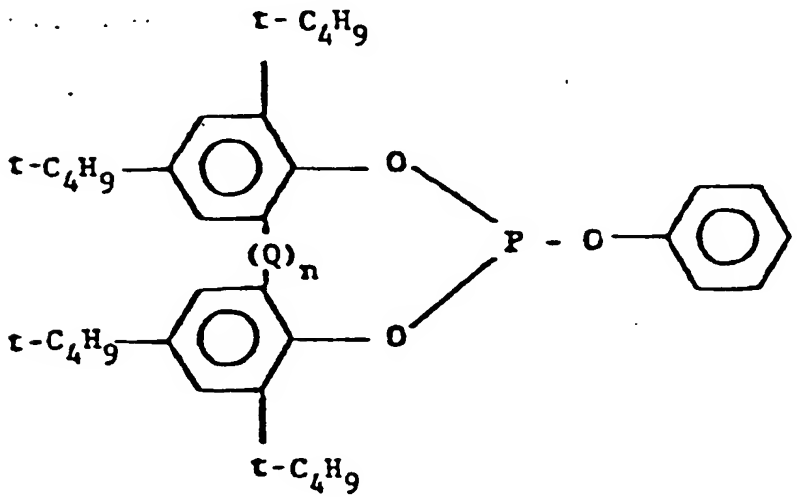
dans laquelle n a la valeur 0 ou 1 ; Q est un groupe $-CH_2-$ ou $-CHCH_3-$; Y^1, Y^2, X^1, X^2, Z^1, Z^2 et Z^3 sont

de l'hydrogène ou ont les définitions données dans la revendication 1 pour les substituants portés par W et Ar, sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 sur un diorganophosphite donné répondant aux formules (III) et (IV) soient des groupes présentant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que dans la formule (III), pas plus de trois des groupes X^1, X^2, Y^1 et Y^2 ne représentent des groupes ayant un encombrement stérique d'isopropyle ou supérieur.

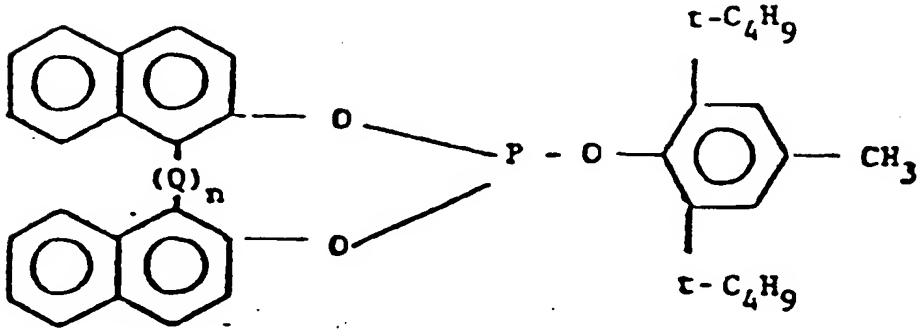
11. Procédé tel que défini dans la revendication 10, dans lequel Y^1 et Y^2 sont des groupes alkyle à chaine ramifiée ayant 3 à 5 atomes de carbone.

12. Procédé tel que défini dans la revendication 10, dans lequel le ligand diorganophosphitique est choisi entre

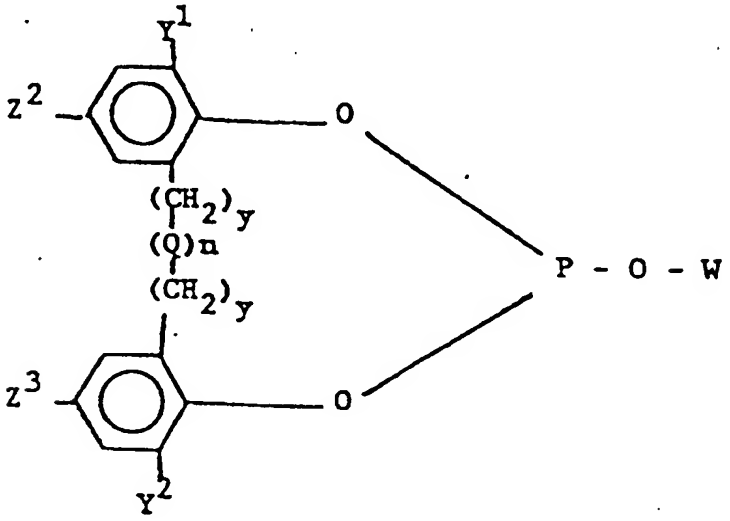




et



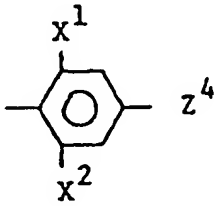
13. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le diorganophosphite complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands répondant à la formule



(V)

dans laquelle Z^2 et Z^3 représentent chacun individuellement un groupe choisi entre le groupe hydroxy et un groupe $-OR^6$; y, n, R^6, Q et W ont la même définition que dans la revendication 1, et Y^1 et Y^2 sont de l'hydrogène ou désignent l'un quelconque des groupes indiqués dans la revendication comme susbstituants de Ar et W.

14. Procédé suivant la revendication 13, dans lequel chaque y a la valeur zéro ; Q est un groupe $-CH_2-$ ou $-CHCH_3-$; R^6 est un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont choisis tous deux individuellement entre l'hydrogène, des groupes alkyle en C_3 à C_{12} à chaîne ramifiée, les groupes phényle, benzyle, cyclohexyle et 1-méthylcyclohexyle ; et W est choisi entre des groupes alkyle en C_1 à C_{18}, des groupes alpha-naphtyle, bêta-naphtyle et un groupe aryle de formule



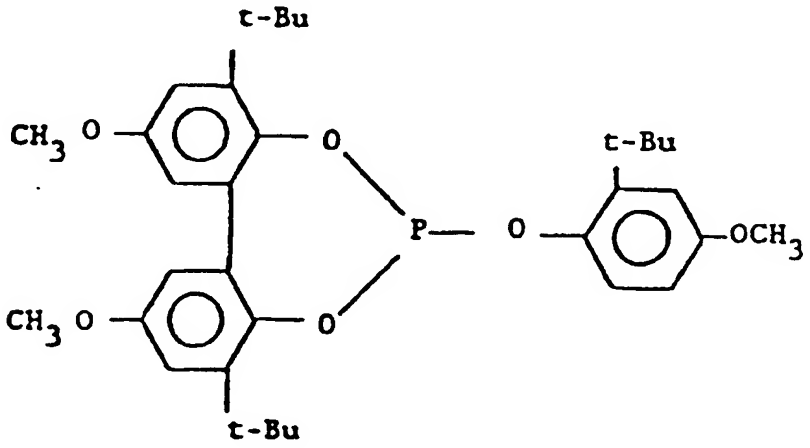
dans laquelle X^1, X^2 et Z^4 sont de l'hydrogène ou l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W, sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 sur un ligand diorganophosphitique donné soient des groupes ayant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que pas plus de trois des groupes X^1, X^2, Y^1 et Y^2 soient des groupes ayant un encombrement stérique d'isopropyle ou supérieur.

15. Procédé suivant la revendication 14, dans lequel Z^2 et Z^3 représentent chacun un groupe $-OR^6$, R^6 représentant un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux des groupes alkyle en C_3 à C_5 à chaîne ramifiée ; et W est un groupe alkyle en C_1 à C_{10}.

16. Procédé suivant la revendication 15, dans lequel Z^2 et Z^3 représentent chacun un groupe méthoxy ; Y^1 et Y^2 représentent chacun un groupe butyltertiaire ; et W représente un groupe méthyle.

17. Procédé suivant la revendication 15, dans lequel n est égal à zéro.

18. Procédé suivant la revendication 13, dans lequel le diorganophosphite complexé avec le rhodium et le ligand diorganophosphitique libre également présent répondent à la formule



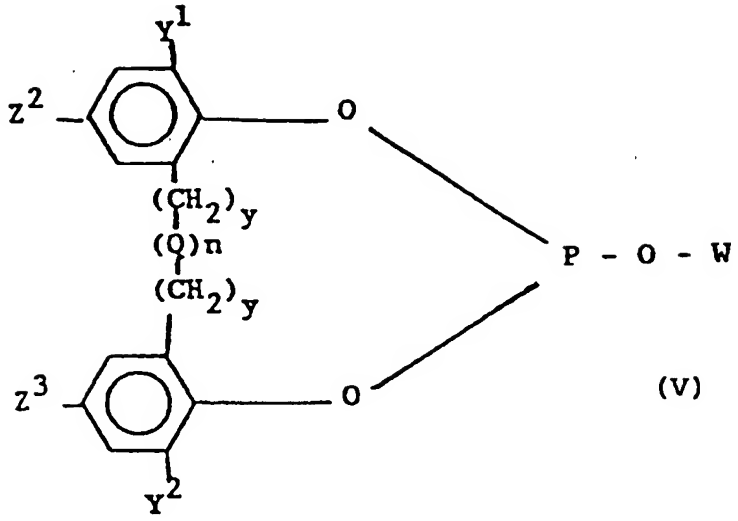
19. Procédé tel que défini dans l'une quelconque des revendications 1 à 18, qui consiste à minimiser la décomposition du ligand diorganophosphitique libre par
(a) enlèvement d'une portion du milieu réactionnel liquide d'hydroformylation de la zone de réaction d'hydroformylation,
(b) traitement du milieu liquide ainsi enlevé avec une résine d'échange anionique faiblement basique et
(c) recyclage du milieu réactionnel traité dans la zone de réaction d'hydroformylation.

20. Procédé tel que défini dans l'une quelconque des revendications 1 à 19, dans lequel l'hydroformylation comprend une opération continue de recyclage de liquide contenant le catalyseur.

21. Procédé tel que défini dans la revendication 20, qui consiste à enlever une portion du milieu réactionnel réactionnel liquide d'hydroformylation de la zone de réaction d'hydroformylation et à faire passer ledit milieu, avant et/ou après que le produit aldéhydique en a été séparé, à travers un lit de résine d'échange anionique faiblement basique.

22. Procédé tel que défini dans l'une quelconque des revendications 19 à 21, dans lequel ladite résine d'échange anionique faiblement basique comprend une résine réticulée d'échange anionique amine tertiaire-polystyrène du type d'un gel ou de type macroréticulaire.

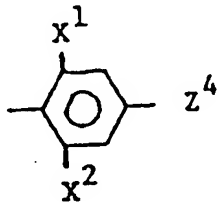
23. Ligand diorganophosphitique répondant à la formule générale



(V)

dans laquelle Z^2 et Z^3 représentent chacun individuellement un groupe choisi entre le groupe hydroxy et un groupe $-OR^6$; y, n, R^6, Q et W ont la même définition que dans la revendication 1, et Y^1, Y^2 représentent l'hydrogène ou l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W, sous réserve qu'au cas où W est un groupe aryle substitué, le ou les substituants soient liés en position para et/ou ortho du groupe aryle par rapport à l'atome d'oxygène qui lie ce groupe aryle à l'atome de phosphore et aussi sous réserve qu'au moins l'un des groupes Y^1, Y^2, Z^2, Z^3 et des substituants d'un groupe aryle W, le cas échéant, ne représentent pas de l'hydrogène et que les positions ortho disponibles sur les groupes aryle présents ne comportent pas toutes un encombrement stérique d'isopropyle ou supérieur.

24. Ligand diorganophosphitique tel que défini dans la revendication 23, dans lequel chaque y a la valeur zéro ; Q est un $-CH_2-$ ou $-CHCH_3-$; R^6 est un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux choisis individuellement entre l'hydrogène, des groupes alkyle en C_3 à C_{12} à chaîne ramifiée, les groupes phényle, benzyle, cyclohexyle et 1-méthylcyclohexyle ; et W est choisi entre des groupes alkyle en C_1 à C_{18}, les groupes alpha-naphtyle, bêta-naphtyle et un groupe aryle de formule



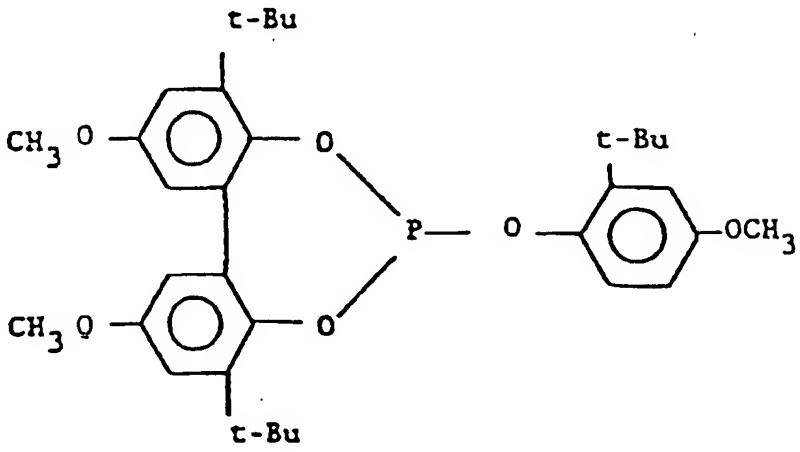
dans laquelle X^1, X^2 et Z^4 représentent l'hydrogène ou l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 portés par un ligand diorganophosphitique donné soient des groupes présentant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que pas plus de trois des groupes X^1, X^2, Y^1 et Y^2 ne soient des groupes présentant un encombrement stérique d'isopropyle ou supérieur.

25. Ligand tel que défini dans la revendication 24, dans lequel Z^2 et Z^3 représentent chacun un groupe $-OR^6$, R^6 représentant un radical alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux des groupes alkyle en C_3 à C_5 à chaîne ramifiée ; et W est un groupe alkyle en C_1 à C_{10}.

26. Ligand tel que défini dans la revendication 25, dans lequel Z^2 et Z^3 représentent chacun un groupe méthoxy ; Y^1 et Y^2 représentent chacun un groupe butyltertiaire ; et W représente le groupe méthyle.

27. Ligand tel que défini dans la revendication 26, dans lequel n est égal à zéro.

28. Ligand tel que défini dans la revendication 23, répondant à la formule



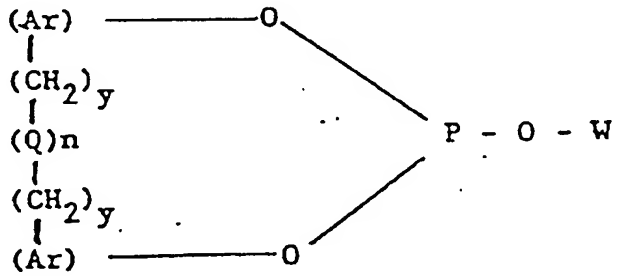
29. Catalyseur d'hydroformylation à base d'un complexe de rhodium, comprenant du rhodium complexé avec un ligand diorganophosphitique tel que défini dans l'une quelconque des revendications 23 à 28.

30. Composition de précurseur catalytique d'hydroformylation à base d'un complexe de rhodium, essentiellement constituée d'un complexe rhodium-diorganophosphite solubilisé, d'un solvant organique et d'un ligand diorganophosphitique libre, caractérisée en ce que le ligand diorganophosphitique dudit complexe et le ligand diorganophosphitique libre sont des ligands tels que définis dans la revendication 1.

31. Composition telle que définie dans la revendication 30, dans laquelle le complexe rhodium-diorganophosphite est un complexe du type acétylacétonate de rhodium-carbonyle-diorganophosphite.

Revendications pour l'Etat contractant suivant : AT

1. Procédé d'hydroformylation pour la production d'aldéhydes, qui consiste à faire réagir un composé organique à non-saturation oléfinique avec l'oxyde de carbone et l'hydrogène en présence d'un catalyseur à base d'un complexe de rhodium essentiellement constitué de rhodium complexé avec de l'oxyde de carbone et un ligand diorganophosphitique, et en présence d'une addition d'un ligand diorganophosphitique libre, caractérisé en ce que le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre sont tous deux, individuellement, des ligands répondant à la formule



(I)

dans laquelle chaque y a individuellement la valeur 0 ou 1 ;
n a la valeur 0 ou 1 ; Q est un groupe divalent de pontage choisi entre $-CH_2-$, $-CH(CH_3)-$ et -S- ;
W est un groupe alkyle en C_1 à C_{18} non substitué ou substitué ou un groupe aryle en C_6 à C_{18} non substitué ou substitué ; et chaque Ar_i représente des groupes aryle non substitués ou substitués

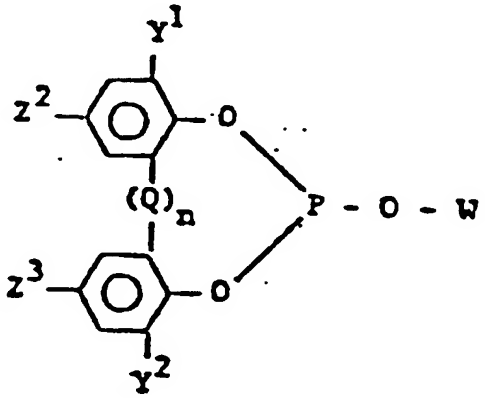
identiques ou différents choisis entre les groupes phénylène, naphtylène et anthracylène ;
le ou les substituants portés par W et Ar étant choisis entre des groupes alkyle en C_1 à C_{18}, phényle, naphtyle, benzyle, phényléthyle, tolyle, xylyle, cyclopentyle, cyclohexyle, 1-méthylcyclohexyle, cyclooctyle, cyclohexyléthyle, halogéno, nitro, cyano, trifluorométhyle, hydroxy, $-Si(R^6)_3$, $-Si(OR^6)_3$, $-N(R^6)_2$, $-C(O)R^6$, $-C(O)OR^6$, $-OC(O)R^6$, $-C(O)N(R^6)_2$, $-N(R^6)C(O)R^6$, $-S(O)_2R^6$, $-S(O)R^6$, $-OR^6$, $-SR^6$, $-P(O)(R^6)_2$ où R^6 représente individuellement des groupes hydrocarbyle identiques ou différents choisis entre des groupes alkyle en C_1 à C_{18} et des groupes aryle, aralkyle, alkaryle et alicycliques contenant 6 à 18 atomes de carbone, sous réserve que dans des substituants $-N(R^6)_2$, les groupes R^6 pris conjointement puissent aussi représenter un groupe divalent de pontage qui forme un groupe hétérocyclique avec l'atome d'azote et que, dans les substituants $-N(R^6)_2$, $-C(O)N(R^6)_2$ et $-N(R^5)C(O)R^6$, les groupes R^6 liés à l'azote puissent aussi représenter de l'hydrogène tandis que, dans les substituants $-P(O)(R^6)_2$, un groupe R^6 puisse aussi représenter l'hydrogène ; les groupes Ar étant liés dans les positions ortho par rapport aux atomes d'oxygène qui lient les groupes Ar à l'atome de phosphore ; et tout substituant, présent sur de tels groupes Ar ou sur un groupe aryle W, étant lié dans la position para et/ou dans la position ortho du groupe aryle par rapport à l'atome d'oxygène qui lie le groupe aryle substitué en question à l'atome de phosphore,
sous réserve que lorsque W est un groupe aryle, l'un au moins desdits groupes aryle Ar et W soit substitué et que le nombre total cumulatif de positions ortho sur Ar et W ne soit pas en totalité substitué avec un radical possédant un encombrement stérique d'isopropyle ou supérieur.

2. Procédé suivant la revendication 1, dans lequel le composé à non-saturation oléfinique est choisi entre des alpha-oléfines contenant 2 à 20 atomes de carbone, des oléfines internes contenant 4 à 20 atomes de carbone et des mélanges de ces alpha-oléfines et de ces oléfines internes.

3. Procédé suivant la revendication 2, dans lequel l'oléfine de départ est choisie entre le butène-1, le butène-2, l'isobutylène et un mélange d'oléfines essentiellement constitué de butène-1 et de butène-2.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel les conditions de la réaction d'hydroformylation comprennent une température de réaction dans la plage de 50 à 120°C, une pression absolue totale du gaz formé d'hydrogène, d'oxyde de carbone et de composé organique à non-saturation oléfinique de 6,9 à 10 340 kPa (1 à 1500 lb/in^2), une pression absolue partielle d'hydrogène de 100 à 1100 kPa (15 à 160 lb/in^2), une pression absolue partielle d'oxyde de carbone de 6,9 à 828 kPa (1 à 120 lb/in^2), et le milieu réactionnel contient 4 à 50 moles dudit ligand diorganophosphitique par mole de rhodium dans ledit milieu.

5. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands répondant à la formule



(II)

dans laquelle Q est un groupe $-CH_2-$ ou $-CHCH_3-$; n a la valeur 0 ou 1 : Y^1, Y^2, Z^2 et Z^3 sont de l'hydrogène ou sont identiques aux substituants portés par Ar et W définis dans la revendication 1, sous réserve que Y^1 er Y^2 soient tous deux des groupes ayant un encombrement stérique d'isopropyle ou supérieur ; et W représente un groupe alkyle en C_1 à C_{18} non substitué.

6. Procédé suivant la revendication 5, dans lequel Y^1 et Y^2 sont des groupes alkyle ramifiés ayant 3 à 5 atomes de carbone et W est un groupe alkyle en C_1 à C_{10} non substitué.

7. Procédé suivant la revendication 6, dans lequel Y^1 et Y^2 sont des groupes tertiobutyle, Q est un groupe $-CH_2-$ et W est un groupe alkyle en C_1 à C_8 non substitué.

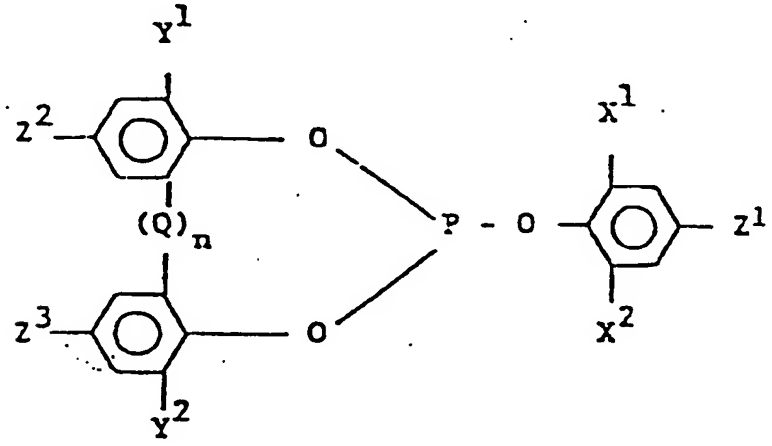
8. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel W est un groupe alkyle à substituant phosphonyle de formule

$$-[C(R^7)_2]_pP(O)(R^6)_2$$

dans laquelle les groupes R^6 sont identiques ou différents et sont choisis individuellement entre des groupes alkyle en C_1 à C_{18}, phényle et cyclohexyle ; les groupes R^7 sont identiques ou différents et chacun est choisi individuellement entre l'hydrogène et des groupes alkyle en C_1 à C_4 ; p est un nombre entier de 1 à 10 ; sous réserve que l'un des groupes R^6 puisse aussi représenter l'hydrogène.

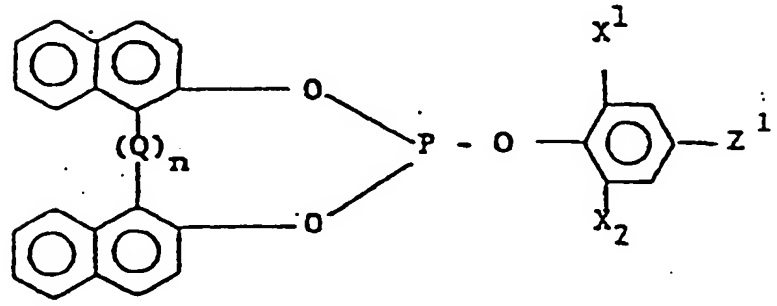
9. Procédé suivant la revendication 8, dans lequel W est un groupe $-CH_2CH_2P(O)(C_6H_5)_2$.

10. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le ligand diorganophosphitique complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands ayant une formule choisie entre



(III)

et



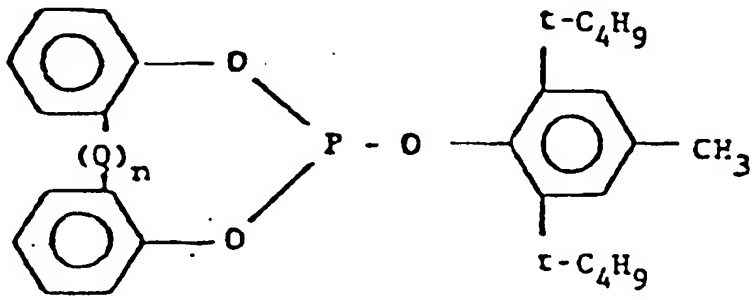
(IV)

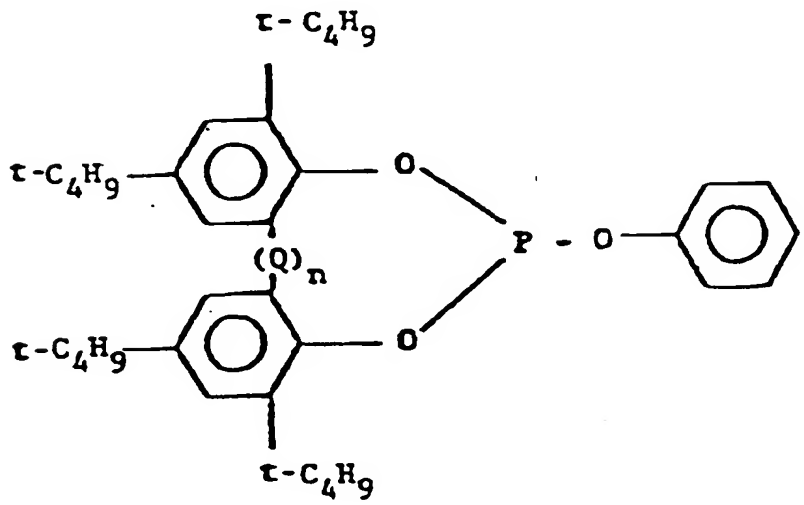
dans laquelle n a la valeur 0 ou 1 ; Q est un groupe $-CH_2-$ ou $-CHCH_3-$; Y^1, Y^2, X^1, X^2, Z^1, Z^2 et Z^3 sont de l'hydrogène ou ont les définitions données dans la revendication 1 pour les substituants portés par W et Ar, sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 sur un diorganophosphite donné répondant aux formules (III) et (IV) soient des groupes présentant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que dans la formule (III), pas plus

de trois des groupes X^1, X^2, Y^1 et Y^2 ne représentent des groupes ayant un encombrement stérique d'isopropyle ou supérieur.

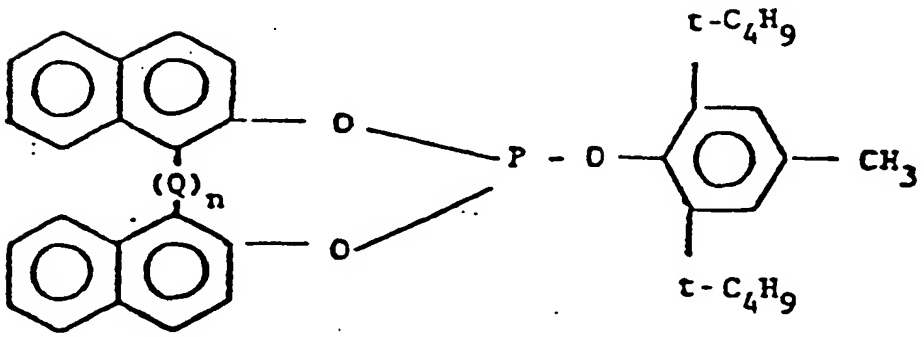
11. Procédé tel que défini dans la revendication 10, dans lequel Y^1 et Y^2 sont des groupes alkyle à chaîne ramifiée ayant 3 à 5 atomes de carbone.

12. Procédé tel que défini dans la revendication 10, dans lequel le ligand diorganophosphitique est choisi entre

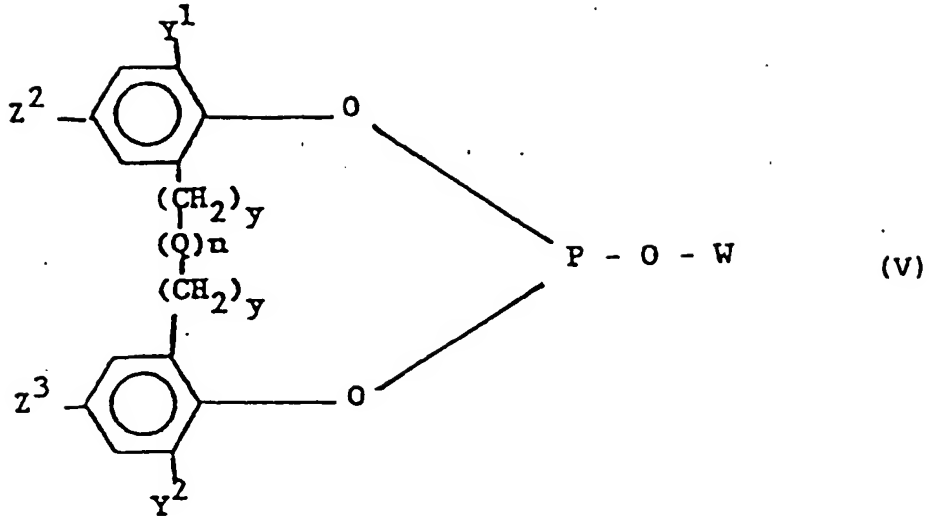




et



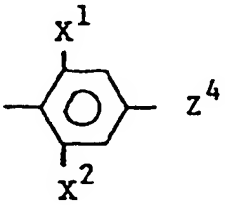
13. Procédé tel que défini dans l'une quelconque des revendications 1 à 4, dans lequel le diorganophosphite complexé avec le rhodium et le ligand diorganophosphitique libre également présent sont tous deux individuellement des ligands répondant à la formule



(V)

dans laquelle Z^2 et Z^3 représentent chacun individuellement un groupe choisi entre le groupe hydroxy et un groupe $-OR^6$; y, n, R^6, Q et W ont la même définition que dans la revendication 1, et Y^1 et Y^2 sont de l'hydrogène ou désignent l'un quelconque des groupes indiqués dans la revendication comme susbstituants de Ar et W.

14. Procédé suivant la revendication 13, dans lequel chaque y a la valeur zéro ; Q est un groupe $-CH_2-$ ou $-CHCH_3-$; R^6 est un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont choisis tous deux individuellement entre l'hydrogène, des groupes alkyle en C_3 à C_{12} à chaîne ramifiée, les groupes phényle, benzyle, cyclohexyle et 1-méthylcyclohexyle ; et W est choisi entre des groupes alkyle en C_1 à C_{18}, des groupes alpha-naphtyle, bêta-naphtyle et un groupe aryle de formule



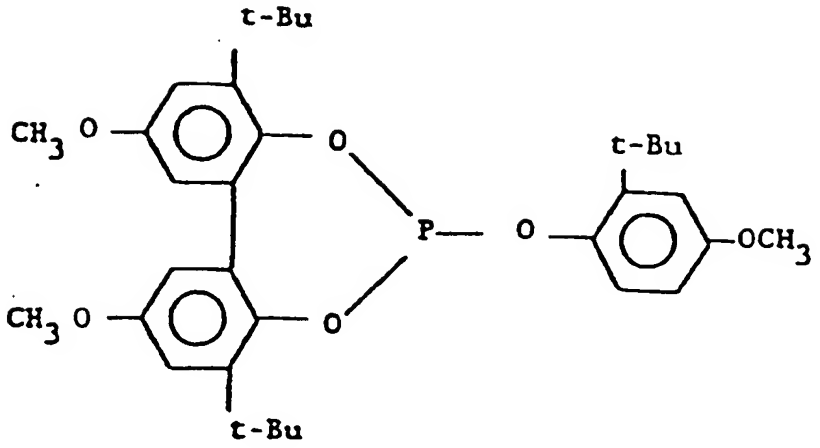
dans laquelle X^1, X^2 et Z^4 sont de l'hydrogène ou l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W, sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 sur un ligand diorganophosphitique donné soient des groupes ayant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que pas plus de trois des groupes X^1, X^2, Y^1 et Y^2 soient des groupes ayant un encombrement stérique d'isopropyle ou supérieur.

15. Procédé suivant la revendication 14, dans lequel Z^2 et Z^3 représentent chacun un groupe $-OR^6$, R^6 représentant un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux des groupes alkyle en C_3 à C_5 à chaîne ramifiée ; et W est un groupe alkyle en C_1 à C_{10}.

16. Procédé suivant la revendication 15, dans lequel Z^2 et Z^3 représentent chacun un groupe méthoxy ; Y^1 et Y^2 représentent chacun un groupe butyltertiaire ; et W représente un groupe méthyle.

17. Procédé suivant la revendication 15, dans lequel n est égal à zéro.

18. Procédé suivant la revendication 13, dans lequel le diorganophosphite complexé avec le rhodium et le ligand diorganophosphitique libre également présent répondent à la formule



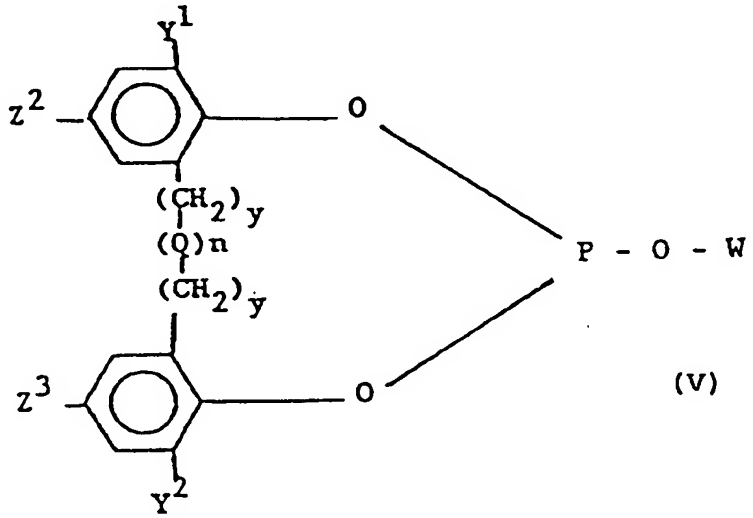
19. Procédé tel que défini dans l'une quelconque des revendications 1 à 18, qui consiste à minimiser la décomposition du ligand diorganophosphitique libre par
(a) enlèvement d'une portion du milieu réactionnel liquide d'hydroformylation de la zone de réaction d'hydroformylation,
(b) traitement du milieu liquide ainsi enlevé avec une résine d'échange anionique faiblement basique et
(c) recyclage du milieu réactionnel traité dans la zone de réaction d'hydroformylation.

20. Procédé tel que défini dans l'une quelconque des revendications 1 à 19, dans lequel l'hydroformylation comprend une opération continue de recyclage de liquide contenant le catalyseur.

21. Procédé tel que défini dans la revendication 20, qui consiste à enlever une portion du milieu réactionnel réactionnel liquide d'hydroformylation de la zone de réaction d'hydroformylation et à faire passer ledit milieu, avant et/ou après que le produit aldéhydique en a été séparé, à travers un lit de résine d'échange anionique faiblement basique.

22. Procédé tel que défini dans l'une quelconque des revendications 19 à 21, dans lequel ladite résine d'échange anionique faiblement basique comprend une résine réticulée d'échange anionique amine tertiaire-polystyrène du type d'un gel ou de type macroréticulaire.

23. Procédé de préparation d'un ligand diorganophosphitique répondant à la formule générale

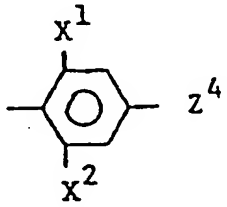


(V)

dans laquelle Z^2 et Z^3 représentent chacun individuellement un groupe choisi entre le groupe hydroxy et un groupe $-OR^6$; y, n R^6, Q et W sont tels que définis dans la revendication 1, et Y^1, Y^2 sont de l'hydrogène ou représentent l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W, sous réserve qu'au cas où W est un groupe aryle substitué, le ou les substituants soient attachés en position para et/ou ortho du groupe aryle par rapport à l'atome d'oxygène qui lie le groupe aryle à l'atome de phosphore et sous réserve également qu'au moins l'un de Y^1, Y^2, Z^2, Z^3 et des substituants portés par un groupe aryle W, le cas échéant, ne représentent pas de l'hydrogène et que toutes les positions ortho disponibles sur les groupes aryle présents ne comportent pas un encombrement stérique d'isopropyle ou supérieur,

procédé qui consiste à faire réagir un composé diphénolique organique correspondant avec le trichlorure de phosphore pour former une phosphorochloridite organique intermédiaire que l'on fait réagir à son tour avec un composé monohydroxylique correspondant en présence d'un accepteur de HCl pour produire le ligand diorganophosphitique désiré.

24. Procédé tel que défini dans la revendication 23, dans lequel chaque y a la valeur zéro ; Q est $-CH_2-$ ou $-CHCH_3-$; R6 est un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux choisis individuellement entre l'hydrogène, des groupes alkyle en C_3 à C_{12} à chaîne ramifiée, les groupes phényle, benzyle, cyclohexyle et 1-méthylcyclohexyle ; et W est choisi entre des groupes alkyle en C_1 à C_{18}, les groupes alpha-naphtyle et bêta-naphtyle et un groupe aryle de formule



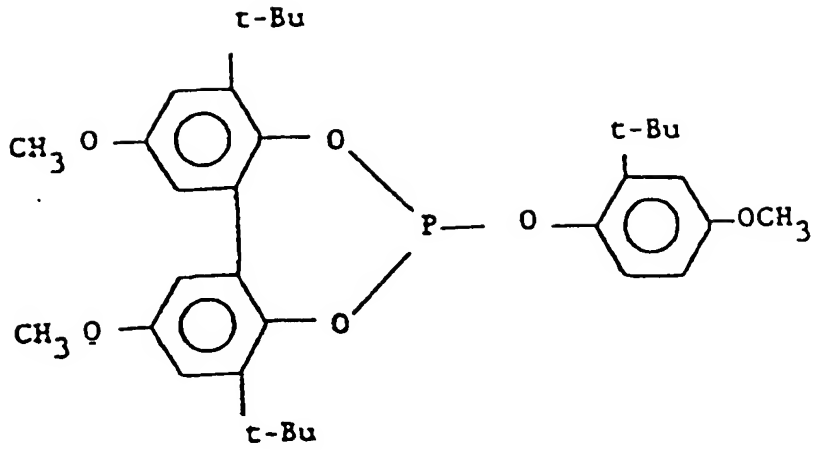
dans laquelle X^1, X^2 et Z^4 sont de l'hydrogène ou représentent l'un quelconque des groupes indiqués dans la revendication 1 comme substituants de Ar et W sous réserve qu'au moins les deux groupes X^1 et X^2 ou qu'au moins les deux groupes Y^1 et Y^2 sur un ligand diorganophosphitique donné soient des groupes présentant un encombrement stérique d'isopropyle ou supérieur, et sous réserve que pas plus de trois des groupes X^1, X^2, Y^1 et Y^2 ne représentent des groupes ayant un encombrement stérique d'isopropyle ou supérieur.

25. Procédé tel que défini dans la revendication 24, dans lequel Z^2 et Z^3 représentent chacun un groupe $-OR^6$, R^6 étant un groupe alkyle en C_1 à C_{10} ; Y^1 et Y^2 sont tous deux des groupes alkyle en C_3 à C_5 à chaîne ramifiée ; et W est un groupe alkyle en C_1 à C_{10}.

26. Procédé tel que défini dans la revendication 25, dans lequel Z^2 et Z^3 représentent chacun un groupe méthoxy ; Y^1 et Y^2 représentent chacun un groupe butyltertiaire ; et W représente le groupe méthyle.

27. Procédé tel que défini dans la revendication 26, dans lequel n est égal à zéro.

28. Procédé tel que défini dans la revendication 23, dans lequel on prépare un ligand répondant à la formule suivante :



29. Catalyseur d'hydroformylation à base d'un complexe de rhodium, comprenant du rhodium complexé avec un ligand diorganophosphitique tel que défini dans l'une quelconque des revendications 23 à 28.

30. Composition de précurseur catalytique d'hydroformylation à base d'un complexe de rhodium, essentiellement constituée d'un complexe rhodium-diorganophosphite solubilisé, d'un solvant organique et d'un ligand diorganophosphitique libre, caractérisée en ce que le ligand diorganophosphitique dudit complexe et le ligand diorganophosphitique libre sont des ligands tels que définis dans la revendication 1.

31. Composition telle que définie dans la revendication 30, dans laquelle le complexe rhodium-diorganophosphite est un complexe du type acétylacétonate de rhodium-carbonyle-diorganophosphite.